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The Discovery of Oxygen

BY

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In ordinary text-books it is customary to dispose of the rival claims of Lavoisier and Priestley cavalierly and in a summary fashion. The former is often held up to public opprobrium as a plagiarist, as one who had heard of the discovery of oxygen from the lips of Priestley himself but forgot to acknowledge his obligations and thus indirectly and by implication, at any rate, claimed it as his own.[2] As this vexed question has been puzzling the brains of many an historian of chemistry for the last century and a half, it is much to be desired that a final and definitive solution, if possible, should be arrived at. We, as Indians—as a third party—can afford to judge the question impartially, for, we do not hold a brief either for the English or for the French and thus can adjudicate between the rival claims.

[1] Presidential address delivered at the Second Annual General meeting of the Indian Chemical Society held at Bombay on the 2nd January, 1926.

[2] "Many of the charges which have been brought against Lavoisier's good faith unfortunately turn out upon investigation to be well-founded, so that whilst wee must greatly admire the clear sight of the philosopher, we cannot feel the same degree of respect for the moral character of the man "—Roscoe and Schorlemmer.

Liebig goes a step further and scarcely even mentions the name of Lavoisier and cites only Black, Cavendish and Priestley among the creators of chemistry, who flourished towards the end of the eighteenth century. Volhard still further improves upon Liebig's verdict. According to him Lavoisier has only appropriated to himself the discoveries of others and has never noticed a new property of a single body. Volhard was evidently smarting under the sting of the well-known passage of Wurtz: "La chimie est une science française." Moreover, he wrote the above in 1870, when the Franco-Prussian war had broken out. It is thus evident that even in a scientific controversy the bias of patriotism comes into play and prevents the formation of a correct estimate of a man's greatness and worth. Kopp also does him but bare justice (*Ges. Chem.*, Vol. 1, p. 306).

Priestley was a born theologian, a controversialist and a linguist to boot. He pursued chemistry simply as a recreation during his leisure hours and as a mere hobby. He had thus to approach the subject without any previous systematic training. As he himself candidly admits : " Had I been anything of a practical chymist, I could not have entertained any such suspicion about mercurius calcinatus on which I had made my experiments." On another occasion in describing the *air from nitre* he says : " This series of facts, relating to air extracted, seem very extraordinary, and important, *and in able hands* may lead to considerable discoveries." Moreover, he had to struggle with poverty, and much of his time was taken up in earning his livelihood as a pastor or tutor. Lavoisier, on the other hand, was born in an opulent family and his father spared no pains to give his son the benefit of a liberal education. He studied mathematics and astronomy, mineralogy and geology as also botany at the feet of eminent professors and was initiated into chemistry by Rouelle, whose fame as an exponent of the science had attracted pupils from far and near. Besides Lavoisier, Rouelle could boast of such illustrious pupils as Bucquet, Bayen, Macquer and Darcet—each and all of whom made their mark as eminent chemists towards the close of the eighteenth century.

There was thus a decided initial advantage on the side of Lavoisier, whose intellectual equipment enabled him to see things in their true perspective. Priestley often improvised his experiments in a crude manner and performed them clumsily and had sometimes to call in the aid of practised hands like Warltire's to be quite sure of the results and to consult professional chemists or apothecaries like Cadet as regards the purity of the red precipitate he used. He was, thus, often led to draw wrong conclusions. We shall select some typical instances to

illustrate the difference in the mental outlook of each of these great precursors of our science.

Lavoisier started his career as a chemist when he was barely twenty-seven, and his first classical experiment (1772) imparted a rude shock to the then current notions about the constitution of matter. From the time of the old Greek and Hindu philosophers it was held that matter was composed of the four (according to the Hindu, five including "byom" or ether) elements and that these were convertible into one another. Chemists had often noticed that when distilled water was evaporated off even in a clean glass vessel there was invariably a solid residue left. This result was vaguely interpreted as the transmutation of water into earth. Lavoisier caused water to be boiled in a specially devised glass vessel for three months, day and night. He weighed the glass vessel very carefully both before and after the experiment as also the evaporated (distilled) water and the residue, and proved conclusively that the weight of the latter was exactly equal to the diminution in weight of the glass vessel—in other words, that the water invariably dissolves a portion of the glass as is now known to every chemist. It should be noticed that *Lavoisier used the balance as his guide in this as in all his subsequent experiments.* He next took up the question of combustibility of diamond. Darcet, Rouelle, Macquer, Boyle, as also the physicists under the patronage of the Grand Duke of Tuscany had already demonstrated that this precious stone when strongly heated on a porcelain dish slowly disappeared.[1] Lavoisier

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[1] There was, however, considerable difference of opinion as regards the cause of this phenomenon, the generally accepted view being that the diamond like phosphorus volatilised away (*vide Hist. Hindu Chem.*, Vol. 1, 2nd Edn p. 101). It was in 1775, i.e., after the discovery of oxygen, that Lavoisier proved that "fixed air is a compound of carbon with the elastic fluid contained in the calx (of mercury)." He then established the identity of diamond with a variety of carbon as the former also, when burnt in oxygen, yielded the fixed air (carbon dioxide).

in collaboration with Macquer and Cadet proved that diamond when prevented from coming into contact with air remained intact and legitimately concluded that it was a case of ordinary combustion like that of charcoal. But the ground was not yet ready for the full and satisfactory explanation, as oxygen had yet to be discovered. This and the succeeding two years were equally eventful. He burnt phosphorus in a closed vessel and found that one-fifth of "the volume of air disappeared and the residual air was unfit for respiration; and knowing the specific gravity of the air he could conclude that this diminution was proportional to the increase in weight of the body burnt. He also proved that sulphur too when burnt, far from losing, gained in weight.

Lavoisier sums up his experiences of 1772 in these memorable words: "Not only sulphur and phosphorus but all bodies, which gain in weight during combustion and calcination, are to be brought under the same category; I am, indeed, inclined to believe that the augmentation in weight of metallic calxes is due to the same cause." [1] Lavoisier now took up in right earnest

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[1] Je crus devoir, dit-il, prendre quelques précautions pour m'assurer la propriété de ma découverte. Il y avait à cette époque une correspondance habituelle entre les savants de France et ceux d'Angleterre · il régnait, entre les deux nations, une sorte de rivalité qui donnait de l'importance aux expériences nouvelles, et qui portrait quelquefois le écrivains de l'une et l'autre nation à les contester à leur veritable auteur. Je crus donc devoir déposer, le 1er novembre 1772, l'écrit suivant, cacheté, entre les mains du secrétaire de l'Académie. Il était conçu en ces termes : "Il y a environ huit jours que j'ai découvert que le soufre, en brûlant, loin de perdre de son poids, en acquérait au contraire; c'est-à-dire qu'une livre de soufre on pouvait retirer beaucoup plus d'une livre d'acide sulfurique, abstraction faite de l'humidité de l'air; il en est de même du phosphore; cette augmentation de poids vient d'une quantité prodigieuse d'air qui se fixe pendant la combustion et qui se combine avec les vapeurs.

"Cette découverte, que j'ai constatée par des expériences que je regarde comme décisives, m'a fait penser que ce qui s'observait dans le soufre et du phosphore pouvait bien avoir lieu a l'égard de tous les corps qui acquièrent du poids, et par la combustion et la calcination, et je me suis persuadé que l'augmentation de poids des chaux métalliques tenait à la même cause"—Grimaux' Lavoisier.

the problem of the increase in weight of lead and tin during calcination. Nearly a century and a half before his time his own countryman, Jean Rey, in 1630, had come to the conclusion that this "increase in weight was due to the fixation of air, which had become thickened and heavy by the vehemence and long continued heat of the fire." [1] Robert Boyle, however, was of opinion—an opinion based upon the old notion of the material nature of fire—that the increase in weight was due to the absorption of the fire particles, which penetrated through the pores of the glass vessel in which the metal was heated. We might profitably recall here the observations of Hooke in this connection.

Hooke distinctly states that "in the dissolution of *sulphureous* (combustible) bodies, by a substance inherent in, and mixed with, the air, which is like, if not the *very same*, with that fixed in saltpetre, a certain part of the bodies is united and mixed, or *dissolved and turned into*, the air, and made to fly up and down with it, in the same manner, as a metalline or other body dissolved into any *menstruum*, doth follow the motions and progress of the *menstruum* till it be precipitated." [2]

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[1] It is of interest to note that Macquer and his collaborator Tillet in 1763 also noticed the increase in weight on calcination. Thus while discussing the increase in the weight of lead on its conversion into litharge, Tillet observes : " It is a true chemical paradox which experience places beyond all doubt ; but if it is easy to state the fact, it is not equally easy to assign a satisfactory reason. It is contrary to all physical ideas."—Hoefer, *Hist. Chim*, II, pp. 386-387.

[2] Hooke further relates : " That whereas *Salt-peter* is a *menstruum*, when melted and red-hot, that abounds more with those Dissolvent particles, and therefore as a small quantity of it will dissolve a great sulphureous body, so will the dissolution be very quick and violent.

Therefore in the *Eleventh* place, it is observable, that, as in other solutions, if a copious and quick supply of fresh *menstruum*, though but weak, be poured on, or applied to the dissoluble body, it quickly consumes it : So this *menstruum* of the Air ; if by Bellows, or any other such contrivance, it be copiously apply'd to the shining body, is found to dissolve it as soon, and as violently as the more strong *menstruum* of melted *Nitre* "—Alembic Club Reprints, *Hooke*, p. 46.

It should be borne in mind in connexion with this, that the Cabbalist and Rosicrucian Fludd, some fifty years before Hooke, held that " the substance of saltpetre is nothing else, but *air* congealed by cold, and he relates that he filled an egg with it, mixed with sulphur and quicklime, and closing the aperture with wax placed the egg under water, where it exploded ". Mayow, who was a contemporary of Boyle, had almost hit upon the true explanation'; only he failed to isolate the particular constituent of the air which took part in combustion. He, in 1668, at the early age of twenty-three, improved upon Hooke and extended his theory to respiration, and affirmed that there is *something in the air* absolutely necessary to life, which is *conveyed into the blood*. Mayow's views, however, received only scant recognition, for the fame of his great contemporaries, Newton and Boyle, " overshadowed the labours of the less well-known investigators." The editors of the " Medico-physical Works of John Mayow" (Alembic Club Reprints) thus remark : " Mayow's works were not much noticed in his own time, and speedily fell into almost total oblivion. ... After the great revolution in chemical theory which followed the discovery of oxygen, Mayow's book was discovered in old libraries, where it had remained disregarded for a hundred years ; and those who discovered it were astonished to see that the new chemistry, which was rapidly conquering the scientific world, was to be found in this old book."

"Curiously enough, while Boyle seems to have read Mayow's work, he does not appear to have been favourably impressed by his conclusions. Boyle, at the age of fifty-two, had, doubtless, formed his own opinions and was unwilling that they should be disturbed by the speculations, well-founded though they were, cf so young a man"—(Ramsay).

The opinion of Boyle, however, prevailed at the time, nay, it was given currency to by the French chemist Lemery whose celebrated treatise, *Course of Chemistry*, was the recognised standard work all along. Lavoisier overthrew this erroneous notion by a simple experiment. He introduced a piece of tin in a closed vessel and weighed it carefully ; it was then placed over a fire and strongly heated. On re-weighing the vessel it was proved that there was only a superficial coating due to the formation of the calx but no loss or gain in weight. He also collected the residual air and found that it had diminished in bulk and was rendered unfit for respiration. Lavoisier thus conclusively proved that the increase in weight of the metal was due to the fixation of a portion of the atmospheric air.

Matters stood thus up till the year 1774. Lavoisier was satisfied that the gain of the metal in weight was due to a portion of the air being fixed but as yet he had no clear conception as to the nature of its particular constituent, which took part in the formation of the calx ; he racked his brains for its isolation but unfortunately the method he adopted proved treacherous.

From time immemorial charcoal had been used in all metallurgical operations for the extraction of the metal from the ores. We all know that it is only a reduction of the oxide of the metal by carbon. The supporters of the phlogistic theory held that as charcoal revived the metal, it simply restored the phlogiston to the calx. In fact charcoal and all carbonaceous matter in general and later on inflammable air (hydrogen) were supposed to be very rich in this imaginary principle. Lavoisier heated a weighed quantity of the calx of lead (minium) and charcoal in a measured volume of air. He obtained the reduced metal and at the same time a volume of a gas which, later on, was identified as carbonic

acid gas; it is this gas which Lavoisier at this stage in his career mistook for oxygen, *i.e.*, the elastic fluid which is fixed in the metal during calcination. It is easy to account for the error into which this great master-mind was led. The reaction, of course, is as follows :

$$Pb_3O_4 + 2C = 3Pb + 2CO_2$$
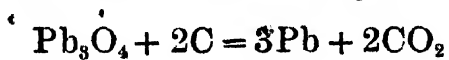
Every tyro in chemistry now knows that carbon dioxide contains its own volume of oxygen but Lavoisier, like his contemporaries, had to grope in the dark. The solution of the vexed problem was now at hand. Fortunately, there exists a metal which, when heated in contact with air, is converted into its calx, and the latter again, when more strongly heated, is reduced to the former metallic state. This peculiar property is shared by the red precipitate or mercurius precipitatus per se. Eck de Sulzbach had already noticed this remarkable phenomenon in 1489 but he failed to draw any conclusion therefrom. Bayen, a fellow-student of Lavoisier, heated a weighed quantity of mercury calx in a retort of known capacity communicating with a receiver of known volume inverted over water. The volume of gas evolved could thus be measured. This he did and he also weighed the metallic mercury formed. He was startled with the result ; here was a calx which, heated by itself without the addition of charcoal to provide the phlogiston necessary for reduction, not only yielded the metal but also a gas. Unfortunately, he did not examine the nature of the gas liberated nor did he even distinguish it from the fixed air obtained on reducing the calx with charcoal, though he noted that the volume of the gas evolved was in both cases approximately the same. Bayen was thus on the eve of a great discovery,

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1 $2HgO = 2Hg + O_2$; $2HgO + C = 2Hg + CO_2$.

There would be as many molecules of oxygen liberated as those of carbon dioxide hence the volumes would be the same.

namely, of oxygen, but he missed it by a hair's breadth. This experiment was conducted in April, 1774. On the 1st of August of the same year Priestley also repeated the same experiment, which we shall allow him to describe in his own words : " With this apparatus, after a variety of other experiments, on the 1st of August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*, and I presently found that, by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express was, that a candle burned in this air with a remarkably vigorous flame. I was utterly at a loss how to account for it........but, however, being at Paris in the October following..........I frequently mentioned my surprise at the kind of air which I had got from this preparation to Mr. Lavoisier, Mr. Le Roy, and several other philosophers who honoured me with their notice in that city, and who, I dare say, cannot fail to recollect the circumstance. *At the same time I had no suspicion that the air which I had got from the mercurius calcina: tus was even wholesome, so far was I from knowing what it was that I had really found. In this ignorance of the real nature of this kind of air, I continued from this time (November) to the 1st of March following.** * *

Till the 1st of March, 1775, I had so little suspicion of its being wholesome, that I had not even thought of applying to it the test of nitrous air; but it occurred to me at last to make the experiment and putting one measure of nitrous air to two measures of this air, I found not only that it was diminished, but that it was diminished quite as much as common air, and that the redness of the mixture was likewise equal to that of a similar mixture of nitrous and common air.* After this I had no doubt

but that the air from *merc. calcinatus* was *fit for respiration*, and *that it had all the other genuine properties of common air*. But I did not take notice of what I might have observed if I had not been so fully possessed by the notion of there being no air better than common air, that the redness was really deeper, and diminution some thing greater, than common air would have admitted. *I now concluded that all the constituent parts of the air were equally and in their proper proportion imbibed in the preparation of this substance, and also in the process of making red lead."* It will thus be seen that in this respect Priestley held exactly the same views as Rey in 1630.

The next step, as Harcourt points out, in Priestley's inquiry was the employment of Mayow's mice, which convinced him that this air was *longer* respirable than common air ; but his ideas of it were less accurate than Mayow's, for instead of considering it, with him, *a constituent part of nitric acid*, he thought it *a compound of nitric acid and earth* ; and in December, 1777, " no doubt remained on his mind that "atmospheric air, or the thing that we breathe, consists of the "nitrous [nitric] acid and earth, with so much phlogiston as is necessary to it's elasticity, and likewise so much more as is necessary to bring it from its state of perfect purity to the mean condition in which we find it " (*Phil. Mag.*, 1846).

We have already seen that Lavoisier was on the lookout for the particular constituent which was responsible for the formation of the calx, but was as yet unsuccessful in separating it from the air and thus proving its individual distinctive property. It was at this very psychological moment that Priestley, who happened to be accidentally at Paris as a companion of Lord Shelburne in his continental tour, in the course of his conversations

with Lavoisier incidentally narrated his own experiences with regard to heating the red calx of mercury. The idea at once flashed across Lavoisier's mind that probably the long looked-for gas was at last in sight. He repeated the experiment and it led to most momentous and epoch-making results—the real explanation of the process of combustion. Lavoisier, in fact, not only isolated oxygen (vital air) but recognised it as a distinct constituent of atmospheric air and systematically explained the part it plays in combustion and respiration, and thus at one bound left Priestley far behind, as will be evident from the latter's recorded opinion in 1775 quoted above.[1] Henceforward, as Hartog tersely puts it, "Lavoisier acted as a sieve to separate the inaccurate work and conclusions of Priestley from the accurate." (Art. on Priestley, *Dict. Nat. Biog.*).

I have devoted some considerable space to the discussion of the question, "Who discovered oxygen?" because the answer cannot be given in one word. It all hinges upon what is really meant by the term discovery. An eminent English chemist writing eighty years ago thus sums up his views: "Whoever may be called the discoverer of oxygen, whether Hooke and Mayow, who first inferred its existence in nitre and in air—or Boyle,

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[1] That Priestley did not, like Lavoisier, keep records of his experiments as is done by ordinary laboratory students and when writing his papers had to draw upon memory—often a deceptive agent—is borne out by his own words : " I cannot, at this distance of time, recollect what it was that I had in view in making this experiment (of extracting 'air' from *mercurius calcinatus*) "—*On Dephlogisticated Air* (Alembic Club Reprints, No. 7. p. 15). As a proof of Lavoisier's unstinted admiration for the English chemists' discoveries of different kinds of " air " may be cited the following. Speaking specially of Priestley he says: " Ce travail, dit Lavoisier en parlant des premiers travaux de Priestley, peut être regardé comme le plus pénible et le plus intéressant qui ait paru depuis M. Hales sur la fixation et le dégagement de l'air. Aucun des ouvrages modernes ne m'a paru plus propre à faire sentir combien la physique et la chimie offrent encore de nouvelles routes à parcourir "—Grimaux, *Lavoisier.*

who first disengaged the elastic gas from minium, or Hales, who collected it from the same material, or Nieuwentyt, who attributed its elasticity to the expansion of the fire particles lodged in the minium, supposing fire to be a particular fluid which maintains its own essence and figure, remaining always fire, though not always burning,—or Priestley who observed that it supported combustion—or Lavoisier who distinguished it as a gas *sui generis*, and determined its principal combinations,—if the question be, which of these names deserves the highest place in the history of this discovery, a philosopher I apprehend might be apt to hesitate—especially perhaps between those which stand *first* in the list, and that which stands *last* "—(Harcourt).

But it was a long time before Lavoisier's views, highly lucid and illuminating though they were, met with universal acceptance. It fact, he had to work alone, single-handed and up-hill for twelve tedious years even after the discovery of oxygen (1774-1786) before his victory was complete. It is remarkable that the " geometers," not being under the tyranny of preconceived notions, were the first to accept Lavoisier's views, whereas the chemists even while admitting the force of his incontestable proofs long hesitated to declare their adhesion to the new doctrine. [1] Berthollet was the first to rally round his banner in 1785 and he was soon followed by Fourcroy and Guyton de Morveau in 1786.

Among the English adversaries there was an eminent chemist, whose authority was held in respect, namely,

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[1] It is generally held that it was the non-French chemists who alone opposed Lavoisier. But this is far from being the case. In a French treatise on chemistry written by Démeste in 1779 the very name of Lavoisier occurs scarcely once. Although chemistry soon came to be designated as the "French science," during the life-time of Lavoisier, at any rate, up till the year 1792, it was not so. In fact, Lavoisier himself protested against this designation. The new chemistry he naturally claimed as his own—"c'est la mienne," as he said.

Kirwan, who attacked Lavoisier's doctrines in his *Essay on Phlogiston*. Madame Lavoisier translated the work into French, and Guyton de Morveau, Lavoisier, Laplace, Monge, Berthollet and Fourcroy subjected this work to a severe criticism chapter by chapter. Kirwan resisted for a time but he was at length so much convinced of the truth of the new doctrine against which he had combated so long that in 1792 he wrote to Berthollet : " I lay down my arms, I abandon the phlogistic doctrine."

While the scientific world was slowly coming round to Lavoisier's views, Priestley could never shake himself free from the trammels of his preconceived notions and always explained the phenomenon of combustion according to his phlogistic theory. Thus a candle when it burnt in air simply disengaged its phlogiston to the air, which *(i e.*, nitrogen *plus* the carbon dioxide), accordingly, was named " phlogisticated air," whereas the same candle or a piece of charcoal burnt longer and more vividly in the " new species of air " (extracted from red calx)—being capable of taking more phlogiston from them it was called " dephlogisticated air." One of his earliest experiments was suggested by the memoir of Cavendish on " Inflammable Air." Cavendish was led to suppose that inflammable air was phlogiston in the free state. In order to test this supposition Priestley placed some minium in a crucible within a tall cylinder filled with inflammable air and inverted over water. He then began to heat the minium by means of a burning lens. " As soon as the minium was dry, by means of the heat thrown upon it I observed that it became black, and then ran in the form of perfect lead ; at the same time that the air diminished at a great rate, the water ascending within the receiver." He concludes " that phlogiston *is* the same thing as inflammable air, and is contained in a combining state in metals, just as fixed

air is contained in chalk and other calcareous substances both being equally capable of being expelled again in the form of air.'ᴏ He could not, of course, detect the formation of water in the process, as he was carrying on his experiment in a jar over water and thus he missed the glory of being the discoverer of the composition of water. Priestley also believed that inflammable air came from iron or zinc when these metals were treated with dilute sulphuric acid, and found an additional experimental support for the view that metals contain phlogiston. To quote Thorpe: " The discovery of oxygen was the death-blow to phlogiston. Here was the thing which had been groped for for years, and which many had even stumbled over in the searching, but had never grasped. Priestley indeed grasped it, but he failed to see the magnitude and true importance of what he had found. It was far otherwise with Lavoisier. He at once recognised in Priestley's new air the one fact needed to complete the overthrow of Stahl's doctrine ; and now, every stronghoid of phlogistonism was in turn made to yield. Priestley, however, never surrendered, even when nearly every phlogistian but he had given up the fight or gone over to the enemy.' When age compelled him to leave his laboratory he continued to serve the old cause in his study, and almost his last publication was the *Doctrine of Phlogiston Established.*"

' The third of the illustrious triumvirate, whose name is indissolubly ' associated with the discovery of oxygen, is Carl Wilhelm Scheele. As an experimenter and discoverer he is simply unrivalled. It has been justly said that he made more discoveries in the course of a dozen years or so than all his contemporary chemists taken together. The claims of Scheele to "the independent discovery of oxygen have never been disputed, and it has now been placed beyond doubt that Scheele

had obtained the gas as early as Priestley's first isolation of it, although his printed account of the discovery appeared about two years after Priestley's. Scheele obtained his "fire-air" by several methods. He heated precipitate of mercury *per se*. He also obtained the gas by heating calxes of silver and gold, as also by treating pyrolusite with oil of vitriol and also by heating nitre. His method of collecting the gas was also peculiar. He used empty bladders for this purpose. Let us give one or two excerpts from his experiments. "I filled a bottle, which contained 10 ounces of water, with this gas. I then placed a small lighted candle in it; scarcely had this been done when the candle began to burn with a large flame, whereby it gave out such a bright light that it was sufficient to dazzle the eyes. I mixed one part of this air with three parts of that kind of air in which fire would not burn; I had here an air which was like the ordinary air in every respect. Since this air is necessarily required for the origination of fire, and makes up about the third part of our common air, I shall call it after this, for the sake of shortness, "fire-air"; but the other air which is not in the least serviceable for the fiery phenomena and makes up about two-thirds of our air, I shall designate after this with the name already known, of Vitiated air." Scheele used as absorbents of the fire air (*i*) oil of turpentine, (*ii*) freshly precipitated ferrous hydroxide, (*iii*) moist iron filings, (*iv*) liver of sulphur, and (*v*) phosphorus. With the aid of these he separated the "other kind of air in which fire would not burn." Scheele had thus no difficulty in proving that "*air must be composed of elastic fluids of two kinds.*" It will be seen that Scheele's views were almost the same as those we hold to-day. But as he was a follower of Stahl, his explanation of the burning of the candle was the same as Priestley's, namely, the

transference of phlogiston to the air, and he was thus led into absurd blunders.   The absorption óf fire-air by liver of sulphur he explained oñ the assumption that heat is a compound of fire-air with Stahl's phlogiston and " that by the action of a double affinity the fire-air in his experiment had combined with the *phlogiston* of the liver of sulphur, and that the compound had passed through the pores of the glass by which it had before been confined."

In the history of scientific discoveries it is often found that chance plays a great part but it should not be taken in the gambler's sense.   As the great Pasteur once said: " In the field of observation chance only favours the mind which is prepared;" in other words the mind must be predisposed towards the reception of new truths, hence the property of the new gas which under " Priestley's observation led to nothing, in the hands of Lavoisier gave rise to one of the most important investigations in the annals of Chemistry "—(Harcourt). Priestley's frame of mind was just the reverse and antithesis of that of Lavoisier as he often based his conclusions on random haphazard experiments To quote his own words: " That more is owing to what we call chance, that is philosophically speaking, to the observation of events arising from unknown causes, than to any proper design or pre-conceived theory in this business."   Eck de Sulzbach is probably the first chemist who in 1489 demonstrated experimentally that the metals increase in weight when calcined; what we now call metallic oxides are named by him fixed ashes of the metal, which is exactly the term used in the Hindu chemical treatises (धातुभस्म).   The mercurius calcinatus *per se* was prepared by him and called fixed mercury; he distinctly says that when the latter is subjected to distillation it disengages a spirit (invisible gas).   He, thus, like Bayen narrowly missed being the discoverer of oxygen.

It has been well said that no single discovery or invention has been made all at once by a single man. unless it be that of logarithms; in fact, there is nothing new under the sun. Every discovery has its origin in the earlier observation of some previous philosopher, but the appellation of the discoverer should best be applied to the man who makes a discovery and elucidates natural phenomena in its light. It now remains for us to conclude with the considered opinions of some more English chemists who have bestowed much thought and study upon the subject. Says Rodwell: "Who is the discoverer? Is it the man who obtains a new body for the first time without recognising that it is different from anything else, or is it the man who demonstrates its true nature and properties...................? If the latter, assuredly Lavoisier discovered oxygen... Priestley's observations read like the writings of the seventeenth century, Lavoisier's like those of the nineteenth. ....Not without reason, said M. Wurtz, "La Chimie est une science française. Elle fut instituée par Lavoisier d'immortelle memoire." [1] The petty jealousies which disfigured the history of science during the end of the last and commencement of the present century (19th) ought to find no place in our minds. The republic of Science is large enough for every man to receive his due." Mr. Pattison Muir reviewing this question observes: "To co-ordinate the facts of science, to describe these facts accurately, to express them in a language which should make it easy to put together facts that were similar and to keep apart those which were unlike, and at the same time to overthrow the phlogistic theory; these were the tasks waiting to be accomplished at the beginning of the last quarter of the eighteenth century. It is not

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[1] Chemistry is a French science. It was founded by Lavoisier of immortal memory.

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often that the power of destroying and the power of reconstructing are united in so extraordinary a degree as they were united in Lavoisier, the greatest of all Chemists."

It will thus be seen that although some English chemists cannot forgive Lavoisier for what is according to them the appropriation of the credit which rightly belongs to Priestley, there are others, on the contrary, in whom the innate sense of justice and fairplay so characteristic of the great nation finds full expression.[1]

It will be instructive here to draw a parallel from the history of the discovery of the composition of water. Cavendish's experiments of 1781 were communicated to Priestley, who had them reproduced with the help of Warltire. But as Priestley was obsessed with the notion that charcoal was very rich in phlogiston, he prepared the latter by heating moist charcoal in a gun-barrel. It will thus be seen that Priestley's so-called phlogiston was a mixture of carbonic oxide and hydrogen—in fact, it was what is now known as water-gas. This is the initial blunder which Priestley and his friend James Watt committed; both these philosophers laboured under the misconception that inflammable air was the same from whatever source it might be obtained. "Priestley's inflammable gas, which he used, cannot have contained

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[1] Thomson in his *History of Chemistry* takes Lavoisier severely to task for his omission of any mention of Priestley's name in connection with the discovery of oxygen, in the paper communicated to the Academy in 1775. He says: "I confess that this seems to me capable of no other explanation than a wish to claim for himself the discovery of oxygen gas, though he knew well that that discovery had been previously made by another." But Thomson seems to contradict himself and almost to give away his case when he says in another place: "It is not the man who forms the first vague notion of a thing that really adds to the stock of our knowledge, but he who demonstrates its truth and accurately determines its nature." Again, "It is obvious, however, that Lavoisier was on the way to make these discoveries, and had neither Scheele nor Priestley been fortunate enough to hit upon oxygen gas, it is exceedingly likely that he would himself have been able to make that discovery."

more than one-fifteenth of its weight of hydrogen and if it had proved anything it would have proved that water consists chiefly of carbon "—(Harcourt). Moreover, Priestley and Watt also accepted the prevailing doctrine of the convertibility of air into water and *vice versa*, and it was on this basis that they explained the formation of water by explosion.

"Cavendish begins his memoir entitled *Experiments on Air*, with an account of a repetition of an experiment of Warltire's related by Priestley, in which a mixture of inflammable air and ordinary air was exploded in a copper vessel, with the result that he observed a loss of a few grains in weight; it is also stated by Warltire that if the explosion took place in a glass vessel it became dewy, which confirmed an opinion, he had long entertained, that common air deposits its moisture by phlogistication."—(Ramsay).

"Cavendish was on the look-out for an explanation as to what had become of "*the air lost*" in the combustion of inflammable air with common air, and he undertook several preliminary trials, by which he searched for the lost gases. He tried (1) whether they were *changed* into carbonic acid; (2) whether they were "*changed*" into nitric acid; (3) whether they were "*changed*" into sulphuric acid; he *negatived* by conclusive experiments these three suppositions of *condensation*; at this crisis of his inquiry Warltire burnt inflammable gas and common air in a vessel which he imagined to be close, and finding a very sensible loss of weight, concluded, with Scheele that ponderable matter had passed through the vessel's pore in the form of heat; at the same time he repeated an observation, made also by others, that in the combustion *water* was deposited from the air, in which he supposed it *to have been contained*: to the mind of Cavendish, deeply meditating what might be the form of

matter into which the *lost airs* could have been *condensed*, this inaccurate experiment immediately suggested the light for which he was watching "—(Harcourt).

There is thus a strong family likeness between the mind of Lavoisier perplexed over the solution of the difficulty regarding the particular constituent of air responsible for combustion and that of Cavendish anxiously intent upon the problem of the disappearance of two volumes of inflammable air and one volume of dephlogisticated air which practically vanished on explosion. Hence, if Priestley were to be credited with the discovery of oxygen, Warltire had still stronger claims to be regarded as the discoverer of the composition of water.

And as regards Watt, Ramsay thus interprets his conception on the matter: "This letter [1] of Watt's [to Black] shows clearly the difference of the two points of view of the new and the old school. While Lavoisier and his followers advanced the view which is now universally accepted, namely, that hydrogen and oxygen, when exploded together, combine to form water and nothing else, Watt was inclined to believe that the water was present in a concealed state in all gases, hydrogen and oxygen among others; and that it was thrown out by the act of combination, and was not the product of the combination." [2] It should be noted here that Watt tenaciously clings to this view even in 1788, although Lavoisier by his crucial

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[1] "I have nothing else new in the philosophical way, except repetitions by Dr. P. of his experiments on the deflagration of D^d [dephlogisticated] and inf'' [inflammable] airs, in [which nitrous acid is always produced. As the deflagrations were performed in copper vessels, the acid is saturated with copper and is green, but becomes blue on the addition of a small quantity of common spirit of nitre. It appears, however, that more than 9/10ths of the liquor thus produced is water, which probably in its own form constitutes the greater part of the mass of all sorts of air. I think it highly probable that the acid proceeds from the inflammable air, and that the D^d [dephlogisticated] air acts the same part that it does in the burning of sulphur and phosphorus."

[2] Ramsay,— *The Life and Letters of Joseph Black*, p. 90.

experiment · in 1783 had satisfactorily established the composition of water.

Here, again, it is necessary to revert for a moment to another much-debated controversy, namely, the priority of the discovery of the composition of water. Cavendish, of course, proved in 1781 by his classical experiments that two volumes of inflammable air and one volume of dephlogisticated air, when exploded by electric sparks, disappeared almost entirely. This is now practically conceded by all parties. As Ramsay says: "These experiments were due to Cavendish; all that Lavoisier did was to show the true nature of the phenomena." But here the question naturally arises—who is the greater of the two—the discoverer of facts or the man who interprets and systematises them? The very experiments of Cavendish when repeated by Lavoisier in conjunction with Laplace, enabled the great French chemist to deal a final blow to the phlogistians. The prevailing belief was that the metals were composed of calx and phlogiston and that on their dissolution in acids the latter was set free and it was even confounded with inflammable air. But Lavoisier now came forward with the true explanation. The metal decomposed the water uniting with its oxygen to form a calx liberating hydrogen; the calx in turn, dissolved in the acid forming a salt. Nay, Lavoisier fortified himself in his position by performing the reverse experiment in collaboration with Meunier. He passed steam over red-hot iron with the result that hydrogen was copiously liberated with the formation of the magnetic iron oxide, *ethiops martial.* Ramsay pathetically exclaims: "It is curious to follow the reasoning which made such an exceptionally acute thinker as Cavendish deliberately reject the true explanation." Ramsay in order to establish or rather vindicate Cavendish's claims naïvely says: "All that Lavoisier did was to

show the true nature of the phenomenon." "Yes, herein lies the greatness of the French chemist. Mellor also evidently inclines to the same view (*vide* J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. I, p. 143).

The controversy, which raged with some degree of bitterness during the life-time of Newton and even after his death over the question of the priority of the invention of fluxions or infinitesimals, may also be mentioned here. Leibnitz, backed by eminent continental mathematicians, claimed it as his own. On the other hand, Newton, or rather his friends maintained with equal pertinacity that the German philosopher, while on a visit to England in 1673, had his hint from Collins to whom Newton had communicated the principles of the method.

While discussing the controversial subject of the discovery of oxygen I have been at the pains to quote the opinions of some eminent English chemists, who, though they have not grudged to vote the major and minor premises, yet, with the exception of one or two, have shrunk from drawing the logical conclusion.

'It is not necessary to belittle the one in order to magnify the other. Each was great in his own way and has extended the boundaries of our science.

Synthesis of Condensed Heterocyclic Systems.

Interaction between 2 : 5-Dithiol-1 : 3 :-4-thiodiazole and Some Organic Dihalides.

BY

PRAFULLA CHANDRA RÂY

AND

BIBES CHANDRA GUHA.

It has been shown by Rây, Guha and Das (*J. Chem. Soc.*, 1919, *115*, 1308) that some mercaptans of the heterocyclic series or rather their potassium salts are singularly reactive towards halogenated organic bodies. They have studied the action of the potassium salts of 2-thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole and 2 : 5-dithiol-1 : 3 :-4-thiodiazole on chloroform, bromoform, iodoform, benzalchloride, monochloracetic acid, ethylene bromide, etc., and have found that condensation is readily effected in almost all these cases. The dithiol, however, could not be made to condense with chloroform, bromoform and iodoform. They observed that monochloracetic acid, benzal chloride and ethylene bromide act upon 2 : 5-dithiol-1 : 3 : 4-thiodiazole but they were unable to isolate the reaction products in a state of purity as they were found to be insoluble in ordinary solvents.

In view of the comparative scarcity of fused heterocyclic systems of the type which would be expected to be produced by the condensation of 2 : 5-dithiol-1 :3 :4-thiodiazole with some reactive dihalides like ethylene

dibromide, benzal chloride and thiophosgene, and also in view of the fact that the dithiol has a curious tendency to form "chain compounds of sulphur". (loc. cit.), it seemed desirable to make another careful study of these condensations and a systematic attempt to isolate the resulting products.

The condensation of the dipotassium salt of the dithiol with ethylene bromide was more fully studied than those with benzalchloride and thiophosgene. It was found that three distinct types of compounds were formed in this reaction.

(i) One molecule of the dimercaptan condensed with one molecule of ethylene bromide thus giving rise to a new mercaptan, $BrCH_2CH_2.S.C_2N_2S.SH$, though with a poor yield. The presence of a free thiol group was proved by the usual tests. Obviously this is the first step in the reaction and the second and third types of products (vide infra) are formed from this intermediate compound.

(ii) One molecule of the dithiol condensed with one molecule of ethylene bromide giving a fused heterocyclic compound, thus;

$$
\begin{array}{c}
N-N \\
\| \quad \| \\
\text{---}C \quad C\text{---} \\
V \\
S \\
\end{array}
$$

| | (I)

S — CH₂ — CH₂ — S
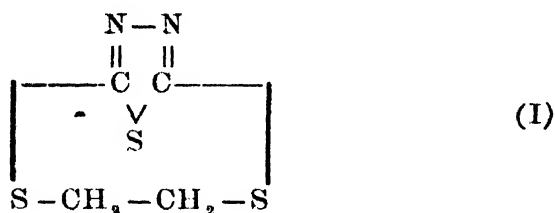
This compound is produced in the largest yield though it will be noticed that one of the component rings consists of seven members of which three are sulphur atoms. Evidently the presence of sulphur contributes to the stability of the ring system.

(*iii*) Several molecules of the dimercaptan and ethylene bromide simultaneously took part in the reaction apparently giving rise to a complex brominated compound, having no mercaptanic property, which could not be purified.

The condensation between molecular proportions of the *dipotassium salt of the dithiol and thiophosgene* produced (1) a crystalline fused heterocyclic compound (II),

$$
\begin{array}{c}
N-N \\
\parallel \quad \parallel \\
-C \quad C- \\
V \\
S \\
\\
S--C--S \\
\parallel \\
S
\end{array}
\qquad (II)
$$
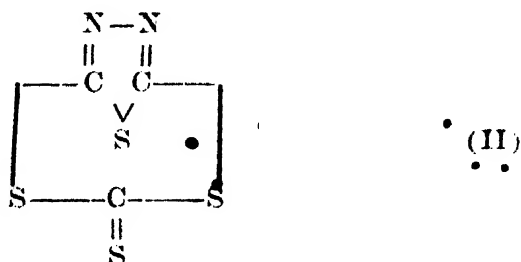
(2) a new dimercaptan of the formula $CS.(S.C_2N_2S.SH)_2$, and (3) a yellow amorphous compound whose identity could not be established.

The reaction between the dipotassium salt and benzal chloride also gave rise to a fused heterocyclic compound of the formula,

$$
\begin{array}{c}
N--N \\
\parallel \quad \parallel \\
-C \quad C- \\
V \\
S \\
\\
S----C----S \\
\wedge \\
H \quad Ph
\end{array}
\qquad (III)
$$
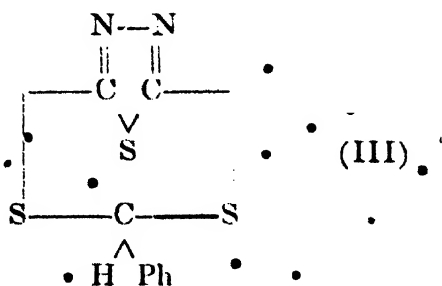
and a dimercaptan of the formula, $CHPh.[S.C_2N_2S.SH_2]$.

The dipotassium salt of the dithiol failed to react with ethylidene chloride even when heated in a sealed tube at 145.° As mentioned above, Ray, Guha and Das noticed that condensation did not take place between 2 : 5-dithiol-1 : 3 : 4-thiodiazole on the one hand and chloroform, bromoform and iodoform on the other, while, curiously

enough, the monomercaptan 2-thiol-5-thio-4-phenyl-
4 : 5-dihydro-1 : 3 : 4-thiodiazole readily condensed with
these. It was suggested therein that probably "the
presence of two SK groups in the dimercaptide exercises
inhibitory influence on the halogen atoms." In order to
test this theory it was attempted to condense both the
free ethylene mercaptan and its disodium salt with
chloroform by refluxing for 10 hours or the water-bath
and by heating in a bomb-furnace at 140° for seven
hours but to no purpose. On the other hand it is well-
known that sodium ethyl mercaptide readily condenses
with chloroform (Gabriel, *Ber.*, 1877, *10*, 185 ; Hoimberg,
ibid, 1907, *40*, 1740) giving orthotrithioformic ethyl ester
CH(SEt)$_3$. Thus the observation that the alkali salts of
both the dimercaptans, dithioethylene glycol and
2 : 5-dithiol-1 : 3 : 4-thiodiazole, are inert towards
chloroform, whereas the alkali monomercaptides of
ethyl mercaptan and 2-thiol-5-thio-4-phenyl-4 : 5-dihydro-
1 : 3 : 4-thiodiazole readily condense with the same
confirms the original suggestion. The above statement,
however, does not appear to contain the whole truth. It
is to be noticed that both the alkali dimercaptides
mentioned above, though inert towards chloroform
ethylidene chloride, etc., readily condense with ethylene
bromide (V. Meyer, *Ber.*, 1886, *19*, 3263). This shows that
halogen atoms attached to the same carbon are probably
less reactive than those that are attached to different
carbon atoms. The presence of negative groups will of
course render the halogen atoms labile even when they
are attached to the same carbon atom. This explains the
condensation of 2 : 5-dithiol-1 . 3 : 4-thiodiazole with
chloropicrin (Râby, Guha, and Das, *J. Chem. Soc.*, 1919,
115, 1309), and with benzal chloride (*vide supra*) and of
ethylene mercaptan with benzal chloride (Râby, *J. Chem.
Soc.*, 1924, *125*, 1142).

EXPERIMENTAL.

Condensation of the Dipotassium Salt of 2 : 5-Dithiol-1 : 3 : 4-thiodiazole with Ethylene Bromide.—Numerous products are formed in this condensation of which only two have been isolated in a pure state after a great many trials. Five gms. of the dipotassium salt were refluxed directly with a considerable excess of ethylene bromide for about 20 hours. After cooling, the mixture was filtered and washed with a little ethylene bromide. The filtrate (*a*) was reserved for future treatment. The residue (*b*) was washed well with alcohol and then rubbed in a mortar several times with water and then filtered. After complete removal of potassium chloride it was washed with a little alcohol and then very gently boiled with ethylene bromide and filtered hot. The filtrate deposited a bluish white mass which was filtered while still warm and washed repeatedly with alcohol. It was recrystallised from boiling ethylene bromide. It is insoluble in all ordinary solvents but soluble in hot tetrachlorethane. It is insoluble in dil. caustic soda. It shrinks above 115° and melts to a viscous green melt at 132-133°. (Found : $S = 54.70$; $N = 15.96$. $C_4H_4N_2S_3$ requires $S = 54.55$; $N = 15.90$ per cent. Absence of bromine was proved.) Its insolubility in ordinary solvents makes it probable that it is a polymeric form of the simple molecule but as it decomposes on continued boiling with ethylene bromide its molecular weight determination is not possible. The filtrate (*a*) was evaporated on the water-bath and air was blown over it to volatilise away the ethylene bromide present. It was then washed several times with cold alcohol. The brown viscous liquid which remained was then taken up three or four times with hot alcohol. The alcoholic solution was evaporated to dryness and again extracted with hot alcohol, the

first and the last fractions being rejected. In this manner after repeated extraction a yellow oil was obtained which gave a yellow precipitate with alcoholic lead acetate. This lead salt of the mercaptan was filtered, washed several times with alcohol and dried. (Found: Pb = 28·61; N = 7·47. $C_8H_8N_4S_6Br_2Pb$ requires Pb = 28·79; N = 7·78 per cent.).

Condensation of the Dipotassium Salt with Thiophosgene.—Seven gms. of the solid were refluxed in benzene solution with 4·4 c.c. of thiophosgene for 15 hours, the condenser being surmounted by a guard tube containing quick-lime. The reaction product was filtered and washed with a little benzene. The filtrate on the addition of a few drops of alcohol and keeping for some time gradually deposited a yellow precipitate which was filtered off and rejected. The filtrate on standing again for some 3-4 hours deposited beautiful yellow needles which were filtered off. The filtrate again, on the addition of a little alcohol and standing, gave a second and a third crop of crystals which were successively filtered off. The filtrate was evaporated to dryness from which by repeated extraction with cold alcohol a new mercaptan was obtained in a tolerably pure state. It was then converted into the lead salt and analysed: (Found: Pb = 38·01; N = 10·81. $C_5N_4S_7Pb$ requires Pb = 37·82; N = 10·23 per cent.) The three crops of crystals mentioned above were 4 or 5 times recrystallised from hot absolute alcohol as colourless needles, m. p. 110-112°. It crystallised with $1\frac{1}{2}$ molecule of alcohol. On keeping for some days in a sulphuric acid desiccator it lost its crystalline shape and turned into a mobile oil. (Found: S = 49·07; C = 28·50; H = 3·35. $C_3N_2S_4$, $1\frac{1}{2}C_2H_5OH$ requires S = 49·04; C = 27·6; H = 3·4 per cent.).

Condensation of the Dipotassium Salt with Benzal Chloride.—Twelve gms. of benzal chloride and 17 gms. of the salt were refluxed in alcoholic solution for 18 hours. Some sulphuretted hydrogen was evolved. The product, after removing benzal chloride by steam distillation, was rubbed in a mortar several times with hot water to remove potassium chloride. The golden yellow solid thus obtained was powdered, taken up several times with hot and cold alcohol and then successively with ether, benzene and acetone, in which it dissolved almost completely. The acetone extract was evaporated to dryness, washed with benzene and then with a little acetone. The residue left behind melted at 195-196°. It is a colourless compound, dissolves completely in cold caustic soda from which it is reprecipitated by hydrochloric acid. Obviously it is a mercaptan. (Found : $N = 14 \cdot 55$; $S = 50 \cdot 15$. $C_{11}H_8N_4S_6$ requires $N = 14 \cdot 50$; $S = 49 \cdot 74$ per cent.) The benzene extract was evaporated, washed with cold alcohol and again taken up with benzene. The benzene product (m. p. indefinite 85-110°) has the composition of the condensed heterocyclic compound (III). (Found : $N = 12 \cdot 07$; $S = 41 \cdot 88$. $C_9H_6N_2S_3$ requires $N = 11 \cdot 8$; $S = 40 \cdot 33$ per cent.) The alcoholic extract contains a mercaptan not identified.

Attempted Condensation with Ethylidene Chloride. The dipotassium salt and an excess of ethylidene chloride were refluxed in alcoholic solution for 10 hours, in benzene solution in a sealed tube on the water-bath, in bomb-furnace without diluent at 140-150° for 6 hours, but to no purpose.

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Synthesis in the Pyrazolone Series. Action of Thiosemicarbazide and 'Semicarbazide on Ketonic Esters.

Part I.

BY

SATISH CHANDRA DE.

The behaviour of hydrazine hydrate towards β-ketonic esters was first investigated by Curtius and Jay (*J. pr. Chem.*, 39, 153) who obtained pyrazolone derivatives of the following type.

$$\begin{matrix} R.CO \\ | \\ CH_2 \\ | \\ COOC_2H_5 \end{matrix} \quad + \quad \begin{matrix} NH_2 \\ | \\ | \\ NH_2 \end{matrix} \quad = \quad \begin{matrix} N=C.R \\ | \quad | \\ HN \quad CH_2 \\ \vee \\ CO \end{matrix} \quad +C_2H_5OH+H_2O$$

$$(I)$$
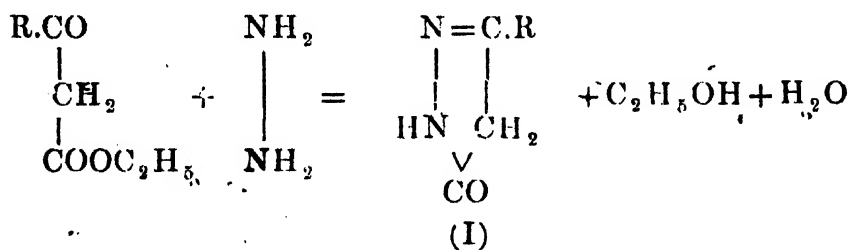
Rothenbúrg then published a series of papers in which he studied the action of hydrazine hydrate on various β-ketonic esters and β-diketones (*J. pr. Chem.*, 52, 23, 45 ; 51, 43, 140, 157 ; etc.). The action of phenylhydrazine and its substitution products on the ketonic esters has long been investigated by a host of investigators who obtained in this way a large number of pyrazolone derivatives.

The present work, a preliminary account of which will be reported here, was undertaken with a view to examine the type of compounds produced by the action of thiosemicarbazide and semicarbazide on the various β-ketonic esters ; and, as might be expected, owing to the

close resemblance in structure between hydrazine, phenylhydrazine, thiosemicarbazide and semicarbazide; the final condensation products of thiosemicarbazide and semicarbazide with acetoacetic ester are quite analogous to those derived from hydrazine and phenylhydrazine.

The carbazides combine readily with acetoacetic ester to give the corresponding semi- and thiosemi-carbazones which part with alcohol on treatment with strong aqueous or alcoholic ammonia in the cold with the formation of pyrazolone derivatives.

$$
\begin{array}{ccc}
N\!\!-\!\!-\!\!-\!\!-\!\!C.CH_3 & & N=C.CH_3 \\
| \quad\quad \diagdown CH_2 & \longrightarrow & | \quad \diagdown CH_2 \\
NH_2.CS(O).\ NH \quad EtO.CO & & NH_2.CS(O).\ N-CO \\
& & (II)
\end{array}
$$
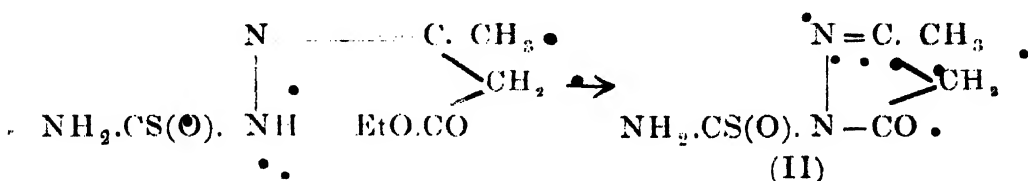
It now requires to be proved whether the acetoacetic ester molecule reacts in its ketonic or enolic form. From the results of his investigation of acetoacetic ester phenylhydrazone .Nef (*Annalen*, 266, 70) came to the conclusion that the resulting compound was not a hydrazone but a hydrazo-compound since by oxidation he was able to isolate an azo-compound from it. The present author has, however, ascribed the hydrazone formulæ to his semi- and thiosemi-carbazones as they could not be oxidised to azo-compounds. Consequently the acetoacetic ester has reacted like a ketone towards semi- and thiosemi-carbazides.

It is a remarkable fact that although the behaviour of both the semicarbazones towards cold ammonia is the same it differs greatly towards heat; for when heated either alone or in presence of water or alcohol the acetoacetic ester semicarbazone gives methylpyrazolone with the elimination of alcohol, ammonia and carbon dioxide whilst the corresponding thiosemicarbazone of acetoacetic ester gives, by such treatment, a derivative of

methylpyrazolone by the elimination of alcohol only. The 3-methylpyrazolone-1-carbamide (II) is stable only in the cold as it splits off the carbamido group with great ease with the formation of 3-methylpyrazolone. The 3-methylpyrazolone-1-thiocarbamide is on the contrary a relatively stable substance which parts with the thiocarbamido group only on prolonged heating.

Both the semicarbazones of acetoacetic ester can react in dilute sodium carbonate solution with another molecule of acetoacetic ester. In this reaction a molecule of water, and a molecule of alcohol are eliminated and the product has formula (III).

$$CH_3 . C = N \qquad CH_3$$
$$H . C \quad N . CS(O). \ N = C - CH_2 . COOC_2H_5 \qquad (III)$$
$$CO$$
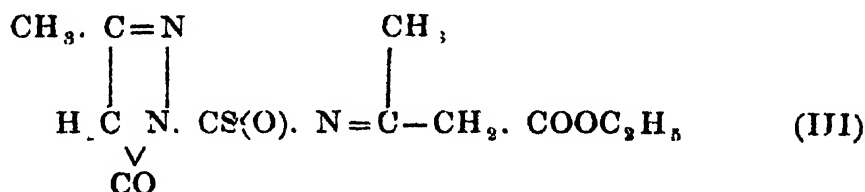
The same product is formed by the action of acetoacetic ester on 3-methylpyrazolone-1 (thio)carbamide. The pyrazolones so obtained give all the reactions as enumerated by Rothenburg. With ferric chloride the pyrazolones give interesting colour reactions which will be described in the proper place.

EXPERIMENTAL.

Condensation of Thiosemicarbazide with Acetoacetic Ester.

(a). *Acetoacetic Ester Thiosemicarbazone.*—When an aqueous solution of thiosemicarbazide hydrochloride (one mol.) was shaken up with acetoacetic ester (one mol.) the thiosemicarbazone separated out after some time (Freund and Schander, *Ber.*, 1902, *35*, 2605); but the reaction takes place much more rapidly with the complete

separation of the thiosemicarbazone on allowing the mixture to react in presence of sodium acetate. The white precipitate so obtained was filtered from the mother-liquor, washed with water and crystallised from benzene. (Found: $N = 20.96$. $C_7H_{13}O_2N_3S$ requires $N = 20.69$ per cent.). With ferric chloride this substance gives no colour reaction. It reduces ammoniacal silver nitrate solution with the evolution of a gas.

(b). *3-Methylpyrazolone-1-thiocarbamide.*—The thiosemicarbazone of acetoacetic ester was covered with strong ammonia and thoroughly stirred when the carbazone gradually went into solution with the evolution of heat; and after some time a small quantity of white needles of the ammonium salt of 3-methylpyrazolone-1-thiocarbamide separated out. This ammonium salt is very unstable as it liberates ammonia even at the ordinary temperature. By the careful addition of acid to the ammoniacal filtrate, the free base could be easily obtained as a voluminous precipitate of white needle-shaped crystals. It was also obtained as white needles by boiling the aqueous solution of its ammonium salt for some time. Crystallised from water it melts at 180°. (Found : $N = 27.01$. $C_5H_7ON_3S$ requires $N = 26.75$ per cent.).

The same compound was obtained when the acetoacetic ester thiosemicarbazone was boiled with water for some length of time. Unlike the corresponding 3-methylpyrazolone-1-carbamide (to be described later) it is very stable and under ordinary conditions does not part with the thiocarbamido group. But by prolonged boiling with water or better by heating with concentrated aqueous or alcoholic potash it splits off the thiocarbamido group and is converted into 3-methylpyrazolone melting at 214°—215° (*J. pr. Chem.*, 39, 52). (Found : $N = 28.78$. $C_4H_6ON_2$ requires $N = 28.57$ per cent.).

It is easily soluble in alcohol and difficultly so- in water and can be conveniently crystallised from water containing a few drops of alcohol. With ferric chloride it gives a deep purple colour.

(c). *3-Methylisopyrazolone-1-thiocarbamide Hydrochloride* was obtained by treating 3-methylpyrazolone-1-thiocarbamide with conc. hydrochloric acid and evaporating the solution to dryness on the water-bath. The residue was washed with absolute alcohol and then with ether. The hydrochloride so obtained is very hygroscopic and melts at 151° (not sharp). (Found : Cl=18·77. $C_5H_7ON_3S$, HCl requires Cl = 18·35 per cent.).

(d). *4:4-Dibromo-3-methylpyrazolone-1-thiocarbamide.*— This compound was obtained by the action of excess of bromine in acetic acid solution on 3-methylpyrazolone-1-thiocarbamide suspended in the same solvent. The pyrazolone gradually dissolved forming a red solution. From acetic acid, in which the dibromo-compound is soluble, a yellowish brown crystalline mass was obtained after neutralisation with sodium carbonate. It is insoluble in the other ordinary organic solvents and was, therefore, purified by dissolving in acetic acid and precipitating with alkali. It melts at 250°. (Found : Br = 50·99. $C_5H_6ON_3SBr_2$ requires Br = 50·79 per cent.).

(e). *4-Bromo-3-methylpyrazolone-1-thiocarbamide.*— The pyrazolone (b) was suspended in acetic acid and bromine (two atoms) dissolved in the same solvent was gradually added. The pyrazolone first dissolved in the acid with the evolution of heat and shortly after the monobromo-derivative separated out in the form of a yellow crystalline mass, which was filtered, washed and finally crystallised from acetic acid in light yellow crystals melting at 220°. (Found : Br = 34·18; N = 18·16. $C_5H_6ON_3SBr$ requires Br = 33·90; N = 17·80 per cent.).

(f). *4-Benzene-azo-3-methylpyrazolone-1-thiocarbamide* was obtained by gradually adding the equivalent quantity of diazotised aniline to the pyrazolone (b) suspended in acetic acid and cooled in ice. The reaction began at once with the evolution of heat and formation of a red solution. The mixture was thoroughly stirred during all the time the diazo-solution was added and then allowed to stand for some time to bring the reaction to completion. The red crystalline solid that separated out was filtered off, washed with water and purified by crystallisation from water when it was obtained in orange crystals melting at 217° with decomposition. (Found: $N = 27 \cdot 07$. $C_{11}H_{11}ON_5S$ requires $N = 26 \cdot 82$ per cent.).

(g). *4-isoNitroso-3-methylpyrazolone-1-thiocarbamide* was obtained either by passing gaseous nitrous acid through the pyrazolone (b) suspended in acetic acid or by adding sodium nitrite solution. The raction began with the separation of a light yellow crystalline mass. This was filtered, washed with water and crystallised from water in yellow needles melting at 180°. (Found: $N = 30 \cdot 39$. $C_5H_6O_2N_4S$ requires $N = 30 \cdot 11$ per cent.).

The *isonitroso* compound has a strong acid reaction. It is soluble in alkalis and from the alkaline solution it can be precipitated by acids. It gives Liebermann's *isonitroso* reaction. The aqueous solution gives with silver nitrate solution an insoluble silver salt of yellow colour.

(h). *3-Methylpyrazolone-1-thiocarbonyl-β-amidocrotonic ester* [1] was obtained when acetoacetic ester (two mols.) and thiosemicarbazide hydrochloride (one mol.) were shaken up with excess of sodium carbonate solution.

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[1] For the sake of convenience the acetoacetic ester has been supposed to react on the urea group of the hydrazone or of the pyrazolone in enolic form (compare Behrend *Annalen*, 229, 5).

Tne liquid was filtered from a small quantity of the un-dissolved hydrazone and the filtrate on acidification with dilute hydrochloric acid gave a white precipitate of 3-methylpyrazolohe-1-thiocarbonyl-β-amidocretonic ester. The same compound was obtained when the freshly pre-pared thiosemicarbazone of acetoacetic ester was shaken with excess of acetoacetic ester in presence of a sufficient quantity of dilute sodium carbonate solutfon. Thus treated the thiosemicarbazone gradually went into solution; the clear solution was allowed to stand for some time and then acidified when a white precipitate was obtained. It was purified by crystallisation from a mixture of alcohol and water when it was obtained in white needles melting at 145°. (Found : $N = 15\cdot82$. $C_{11}H_{15}O_3N_3S$ requires $N = 15\cdot61$ per cent.).

It is almost insoluble in cold water and alcohol but dissolves readily in hot alcohol. With ferric chloride, it gives a beautiful deep indigo-blue coloration. It is very stable towards heat in presence of ordinary solvents but on prolonged boiling with water or alcohol it decomposes into acetoacetic ester and 3-methylpyrazolone-1-thiocar-bamide. A solution of the substance gives with silver nitrate an insoluble silver salt.

Condensation of Semicarbazide with Aceto-acetic Ester.

(a). *Acetoacetic Ester Semicarbazone.*—The method of preparation of this compound is the same as that for the corresponding thiosemicarbazone of acetoacetic ester. A mixture of acetoacetic ester (one mol.), semicarbazide hydrochloride in aqueous solution (one mol.) and sodium acetate was shaken. After some time the semicarbazone separated out in the form of a white amorphous powder; this was filtered, washed with water

and then crystallised from ether.. (Found : N=22·62. C$_7$H$_{13}$O$_3$N$_3$ requires N = 22·46 per cent.).

The semicarbazone of acetoacetic ester crystallises from ether in beautiful white needles melting at 129°. It is easily soluble in hot water and alcohol. It gives no colour reaction with ferric chloride. It reduces ammoniacal silver nitrate solution with the evolution of a gas; mercuric oxide is also reduced by the boiling aqueous solution of the hydrazone. When this semicarbazone was heated at 115°—120° it evolved ammonia gas and at the same time turned brown. The temperature was maintained at 120°—125° for several hours till no more ammonia gas was evolved. The residue was then extracted with hot water, boiled with charcoal and from the filtrate a white crystalline substance was obtained melting at 214—16°, which is identical with 3-methylpyrazolone of Curtius (loc. cit.). The same compound was also obtained when the semicarbazone was boiled with water.

(b). *3. Methylpyrazolone-1-carbamide.*—For the preparation of this compound the above semicarbazone was shaken with ammonia solution and allowed to stand for some time after which the liquid was filtered from any undissolved semicarbazone. From the filtrate the pyrazolone was precipitated by acid as a white crystalline mass. This was dissolved for purification in the least quantity of methyl alcohol and precipitated by ether. It melts at 192°. (Found.: N = 30·12. C$_5$H$_7$O$_2$N$_3$ requires N = 29·79 per cent.).

It is moderately soluble in cold water and alcohol and insoluble in ether. With ferric chloride it gives a blue coloration. By gentle warming of its aqueous or alcoholic solution, it easily parts with the carbamido group and forms 3-methylpyrazolone.

(c). *3-Methylisopyrazolone Hydrochlorida.*—3-Methyl-pyrazolone-1-carbamide combines very easily witn acids and bases to form unstable salts. When treated with concentrated hydrochloric acid and ,the solution evaporated to dryness, a residue was obtained which was extracted with absolute alcohol. From the alcoholic solution a light yellow coloured oil separated out by the addition of ether. This oil was separated and allowed to stand in vacuum over sulphuric acid when it solidified to a crystalline mass of *3-methylisopyrazolone hydrochloride*. It is extremely hygroscopic. (Found: $N = 23 \cdot 97$; $Cl = 20 \cdot 31$. $C_5H_7O_2N_3$, HCl requires $N = 23 \cdot 66$; $Cl = 20 \cdot 0$ per cent.).

The ammonium salt of 3-methylpyrazolone-1-carbamide could not be obtained in the solid state. By evaporation of its ammoniacal solution in vacuum over sulphuric acid the free base was obtained, The salt is stable in solution and its aqueous solution gave with silver nitrate a white precipitate of the silver salt, which is much more stable than 3-methylpyrazolone-1-carbamide itself, but when long boiled with water it liberated the carbamido group and passed into the silver salt of 3-methylpyrazolone. (Found: $Ag = 53 \cdot 32$ $C_4H_5ON_2Ag$ requires $Ag = 52 \cdot 68$ per cent.).

(d). *4:4-Dibromo-3-methylpyrazolone-1-carbamide* was obtained by treating the pyrazolone (b) dissolved in methyl alcohol with a slight excess of bromine in acetic acid solution. The reaction began with the evolution of heat. From the acid solution the dibromo-compound was obtained by neutralisation with alkali. It is insoluble in most organic solvents and was therefore purified by dissolving in acetic acid and precipitating with alkali. It melts at 225°. (Found: $Br = 53 \cdot 74$. $C_5H_5O_2N_3Br_2$ requires $Br = 53 \cdot 51$ per cent.). When the dibromo-

derivative was long boiled with water, it was converted into another substance melting at 184° and was found to be identical • with the dibromo-3-methylpyrazolone of Rothenburg • (*J. pr. Chem.*, 52, •37). (Found: Br = 62·74. $C_4H_4ON_2Br_2$ requires Br = 62·50 per cent.).

(e). *4-Benzene-azo-3-methylpyrazolone-1-carbamide* was obtained in the form of a reddish brown crystalline mass by adding the calculated quantity of diazotised aniline to the methyl alcoholic solution of the pyrazolone (b). This was filtered off, washed and crystallised from alcohol. It melts at 235°. (Found.: N = 28·86. $C_{11}H_{11}O_2N_5$ requires N = 28·57 per cent.). On long continued boiling it suffers decomposition and forms 4-benzene-azo-3-methylpyrazolone melting at 195-97°.

(f). *4-isoNitroso-3-methylpyrazolone-1-carbamide* was obtained by passing gaseous nitrous acid through the methyl • alcoholic solution of the pyrazolone. The solution was first coloured red and a yellow crystalline precipitate was formed which was filtered off, washed first with water and then with hot alcohol to free it from any unchanged starting material. It melts at 210° and is sufficiently pure for analysis. (Found : N = 33·32. $C_5H_6O_2N_4$ requires N = 32·94 per cent.).

It is insoluble in organic solvents but on long boiling with water it gradually dissolves. The aqueous solution on cooling deposits crystals of 4-isonitroso-3-methyl-pyrazolone of Curtius and Rothenburg and is evidently formed by the elimination of the carbamido group from the above 4-isonitroso compound. The isonitroso-compound has a strong acid reaction and dissolves readily in alkalis from whose solution it can be precipitated by acids. An ammoniacal solution of the substance gives with silver nitrate a yellow precipitate of the isonitroso-silver salt.

(g). *3-Methylpyrazolone - 1 - carbonyl - β-amidocrotonic ester* was obtained by a method analogous to that described for the corresponding thiocarbonyl compound either from acetoacetic ester (two mols.) and semicarbazide hydrochloride (one mol.) or from acetoacetic ester semicarbazone and the ester, in presence of dilute sodium carbonate solution, the substance being precipitated from the carbonate solution by dilute hydrochloric acid. For purification it was dissolved in cold sodium carbonate solution and re-precipitated by acid in white needles melting at 175-6° with decomposition. (Found : $N = 16 \cdot 91$. $C_{11}H_{15}O_4N_3$ requires $N = 16 \cdot 60$ per cent.).

It is insoluble in cold benzene, water and alcohol. It gives a deep blue coloration with ferric chloride. It is very unstable towards heat. When boiled with water it gradually dissolves with the evolution of ammonia and liberation of an oil floating on the water which was identified as acetoacetic ester and from the clear solution crystals of 3-methylpyrazolone were obtained. A methyl alcoholic solution of the substance gives with silver nitrate a silver salt in light yellow gelatinous form.

Further work on this line is in progress and will form the subject of a subsequent communication.

I avail myself of this opportunity of expressing my gratitude to Dr. J. C. Ghosh and Dr. P. C. Guha for the kind interest they have taken in this investigation.

ortho-Aminophenylhydrazine and Some Interesting Heterocyclic Compounds : derived from It.

Part II.

Synthesis of Azoles, Azines, Heptazines and Octazines*

BY

PRAPHULLA CH. GUHA AND MAHENDRA K. DE.

o-Aminophenylhydrazine was prepared in this laboratory last year by Guha and Ray and its actions upon benzaldehyde, potassium ethyl xanthate, urea, mustard oils, etc., were studied (this *Journal*, 1925, **2**, 83). With the object of synthesising poly-membered heterocyclic compounds, it has now been condensed with o-diketones, monoximes of o-diketones, diamines, esters and chlorides of dicarboxylic acids and thiosemicarbazide, and in every case the above expectation has been fully realised.

o-Aminophenylhydrazine reacts with benzil to give 2 : 3-benzo-5 : 6-diphenyl-1 : 4 : 7-heptatriazine, thus :

$$\begin{array}{c} \text{Ph.CO} \\ | \\ \text{Ph.CO} \end{array} + \begin{array}{c} \text{NH}_2.\text{NH} \\ \\ \text{NH} \end{array} >C_6H_4 = \begin{array}{c} \text{Ph.C=N.NH} \\ | \\ \text{Ph.C} \underline{\quad\quad} \text{N} \end{array} >C_6H_4 + 2H_2O$$

(I)
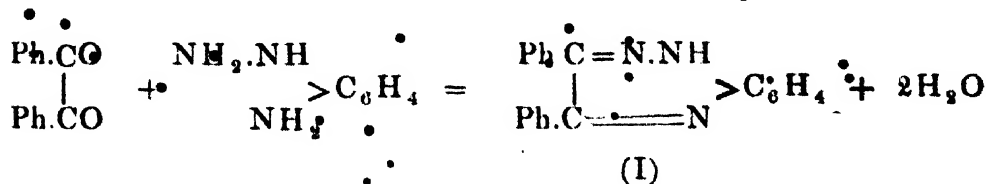
Four more hepta-triazine compounds have similarly been obtained from alloxan, isatin, acenaphthaquinone and phenanthraquinone (compare Thiele and Stanger, *Annalen*, **283**, 1; Nietzki, *Ber.*, 1895, **28**, 1357; Tauber,

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Ber., 1892, *25*, 3287; Niementowsky, *Ber.*, 1901, *34*, 3334 ; Cain, *J. Chem. Soc.*, 1914, *105*, 1440 ; 1920, *117*, 1143 ; Hinsberg, *Annalen*, *292*, 245 ; *Ber.*, 1896, *29*, 200 ; *Annalen*, *237*, 340 ; Marchlewsky and Buraczewsky, *Bull. Acad. Sci., Cracow,* 1900, 374; Schmidt and Soll, *Ber.*, 1908, *41*, 3696). Monoximes of isatin and phenanthraquinone give rise to interesting octa-triazine compounds, thus:

$$-CO \atop -C \text{ NOH} \quad + \quad NH_2.NH \atop NH_2 > C_6H_4 \quad = \quad -C=N.NH \atop -C=N.NH > C_6H_4 + 2H_2O$$

<div align="center">(II)</div>
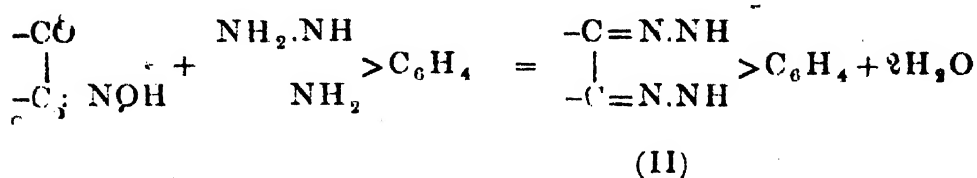
The above reactions differ remarkably from that observed by Schmidt and Glatz (*Ber.* 1911, *44*, 276) who observed the elimination of hydroxylamine and water and not two molecules of water as in the present instance.

Two molecules of ammonia escape from one molecule of *o*-phenylenediamine and one molecule of the aminohydrazine with the formation of 2 : 3 : 6 : 7-dibenzo-4 : 5-dihydro-1 : 4 : 5-heptatriazine, thus:

$$C_6H_4 < {NH.NH_2 \atop NH_2} \quad + \quad {NH_2 \atop NH_2} > C_6H_4$$

$$= \quad C_6H_4 < {NH.NH \atop NH} > C_3H_4 \quad + 2NH_3$$

<div align="center">(III)</div>
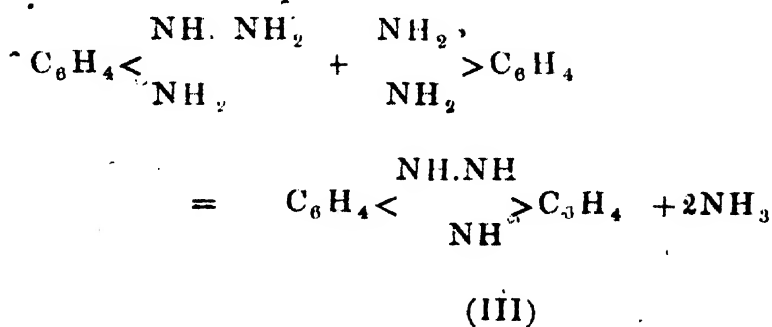
(Compare Pinner, *Ber.*, 1887, *20*, 2358; Fischer and Hepp, *Ber.*, 1890, *23*, 2791; Arndt and Bielich, *Ber.*, 1923, *56*, 809 ; Guha and De, this *Journal*, 1925, *1*, 144).

A controversy may arise here, *viz.*, the *imino* instead of the *amino* group of the hydrazine residue might react as well to give rise to a *N*-aminophenazine compound, thus:

$$C_6H_4 < {\overset{\overset{NH_2}{\underset{\displaystyle N}{|}}}{} \atop NH} > C_6H_4$$
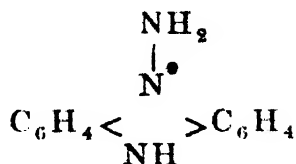
But, as the compound does not react with benzaldehyde or mustard oils, the *N*-aminophenazine type of formula has been dispensed with. 1:3:4-Tolylene- diamine and 1:2-naphthylenediamine similarly give a benzo-methylbenzo-heptatriazine and a benzo-naphthoheptatriazine respectively.

Oxalyl chloride yields *o*-phenylene semioxamazide, thus:

$$C_6H_4 < {NH.NH_2 \atop NH_2} + {COCl \atop COCl} = C_6H_4 < {NH-NH.CO \atop NH CO} + 2HCl$$

(IV)
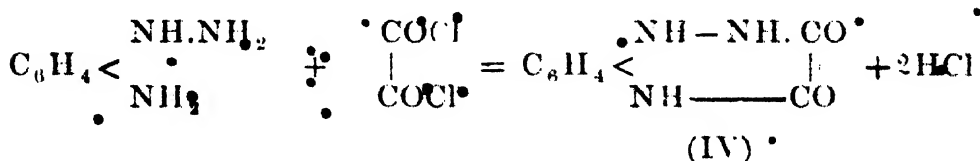
Diethyl malonate yields *o*-phenylene-semimalonamazide. (Meyer, *Annalen*, 327, 14, 26; 347, 25, 34; 415, 33, 42):

$$C_6H_4 < {NH.NH_2 \atop NH_2} + {EtO.CO \atop EtO.CO} > CH_2 = C_6H_4 < {NH.NH.CO \atop NH.CO.CH_2}$$

(V)
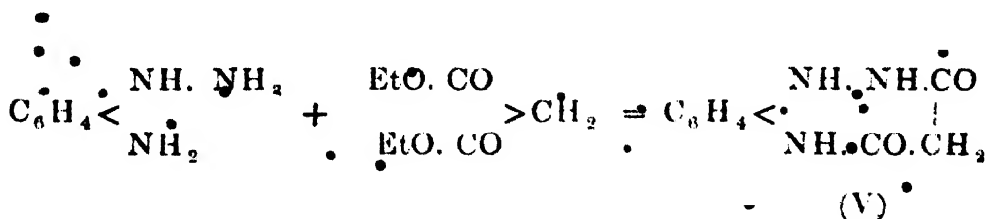
One molecule of thiosemicarbazide reacts with one molecule of the aminohydrazine with the liberation of two molecules of ammonia forming a compound of

composition $C_7H_8N_4S$ which may be represented by any of the following four formulæ.

$$C_6H_4 <^{NH.NH_2}_{NH_2} + ^{NH_2}_{NH_2.NH} >CS \longrightarrow C_6H_4 <^{NH.NH}_{NH.NH} >CS$$

$$(VI\ a)$$

$$\text{or}\quad C_6H_4 <^{N(NH_2)}_{NH.NH} >CS$$

$$(VI\ b)$$

$$C_6H_4 <^{NH.NH_2}_{NH_2} + ^{NH_2}_{HS} >C:N.NH_2$$

$$= C_6H_4 <^{NH - NH}_{\underline{\quad}S\underline{\quad}} >C:N\cdot NH_2$$

$$(VI\ c)$$

$$C_6H_4 <^{NH.NH_2}_{NH_2} + ^{HS}_{NH_2.NH} >C:NH = C_6H_4 <^{NH - S}_{NH.NH} >C:NH$$

$$(VI\ d)$$
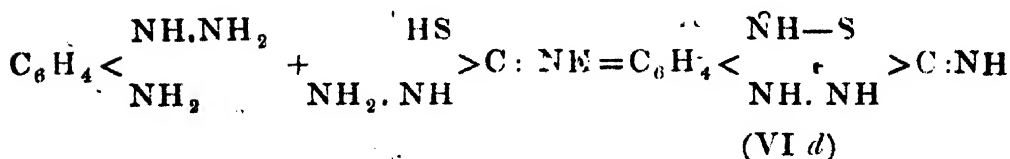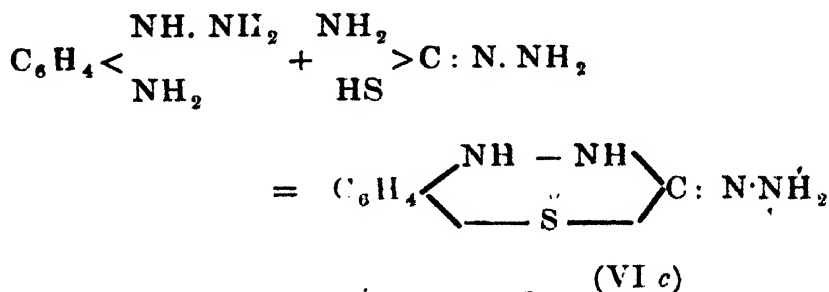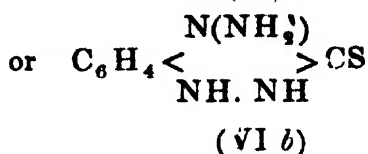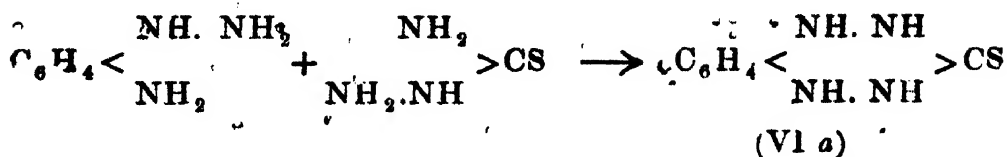
The compounds of formulæ (VIc) and (VId) should be strongly basic, but the product is acidic in nature, forms alkali salts which form lead and mercury mercaptides, and a disulphide. All these facts are in harmony with the formulæ (VIa) and (VIb). But formula (VIb) has been rejected on the ground that the compound does not dissolve in hydrochloric acid and does not form any compound with benzaldehyde.

o-Nitrophenylhydrazine does not appear to possess any capacity to form any closed-ring compound with aldehydes, ketones, amines, esters, etc., as the aminohydrazine. It can, however, form open-chain compounds

with these reagents and the nitro group of the resulting product can be reduced to an amino group which at once creates a possibility for ring-closure.

Acetaldehyde-*o*-nitrophenylhydrazone yields μ-methyl-benziminazole on reduction (compare Franzen, *Ber.*, 1907, *40*, 909; Guha and Ray, this *Journal*, 1925, *1*, 193).

o-Nitrobenzaldehyde- and salicylaldehyde -*o*-nitro-phenylhydrazones, when reduced with tin and hydrochloric acid, do not yield μ-aminophenyl- and μ-hydroxy-phenyl-benziminazoles as might be expected by analogy with the foregoing reaction, but 2 : 3 : 7 : 8-dibenzo-1 : 5 : 6-octatriazine and 2 : 3 : 7 : S-dibenzo-1 : 5 : 6-octaoxydiazine are formed, thus :

$$C_6H_4 <_{NH.\ N=CH}^{NO_2\quad O_2N} >C_6H_4 \longrightarrow C_6H_4 <_{NH.\ N=CH}^{NH_2\quad H_2N} >C_6H_4$$

$$\longrightarrow C_6H_4 <_{NH.\ N=CH}^{-NH-} >C_6H_4$$
$$(VII)$$

$$C_6H_4 <_{NH.\ N=CH}^{NO_2\quad HO} >C_6H_4 \longrightarrow C_6H_4 <_{NH.\ N=CH}^{NH_2\quad HO} >C_6H_4$$

$$\longrightarrow C_6H_4 <_{NH.\ N=CH}^{-O-} >C_6H_4$$
$$(VIII)$$
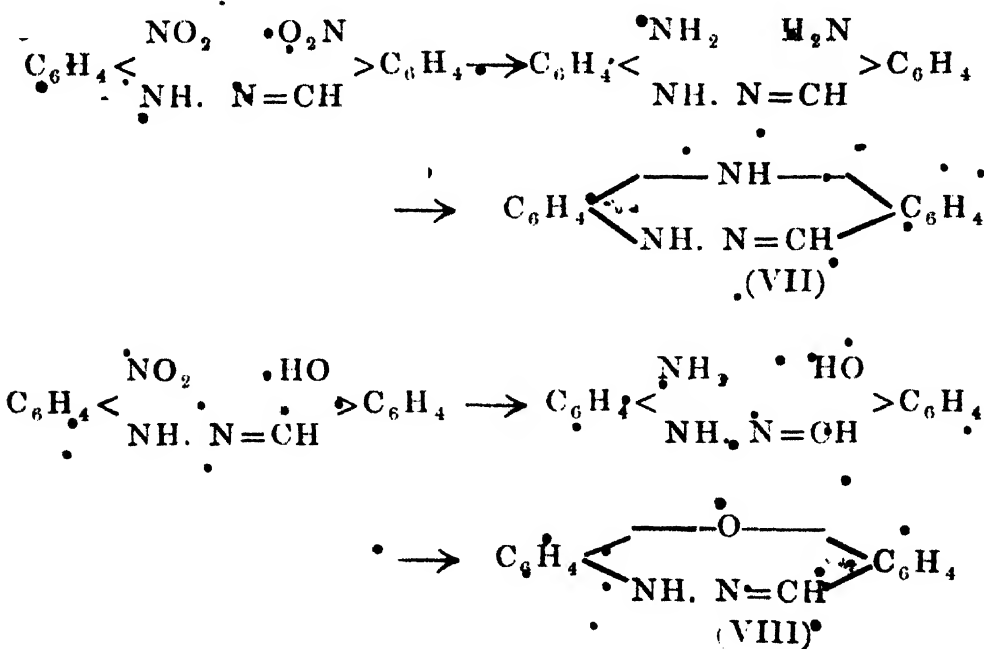
The reason for assigning formula (VII) to the nitrobenzaldehyde compound is that it does not give any reaction of the amino group. The formula (VIII) has been retained on similar grounds, *viz.*, because it does not respond to any hydroxylic reactions.

Acenaphthaquinone, anthraquinone, α-naphthaquinone and phenanthraquinone give the corresponding mono-nitrophenylhydrazones and the first one has been utilised for synthesising a seven-membered ring-compound, 2 : 3-benzo-5 : 6-acenaphtho-1 : 4 : 7-heptatriazine, thus :

$$C_{10}H_6 < \overset{CO}{\underset{CO}{|}} \longrightarrow C_{10}H_6 < \overset{C=N.\ NH}{\underset{CO \quad O_2N}{|}} > C_6H_4 \longrightarrow$$

$$C_{10}H_6 < \overset{C=N.\ NH}{\underset{CO \quad H_2N}{|}} > C_6H_4 \longrightarrow C_{10}H_6 < \overset{C=N.NH}{\underset{C=\!=\!=N}{|}} > C_6H_4$$

<div align="center">(IX)</div>
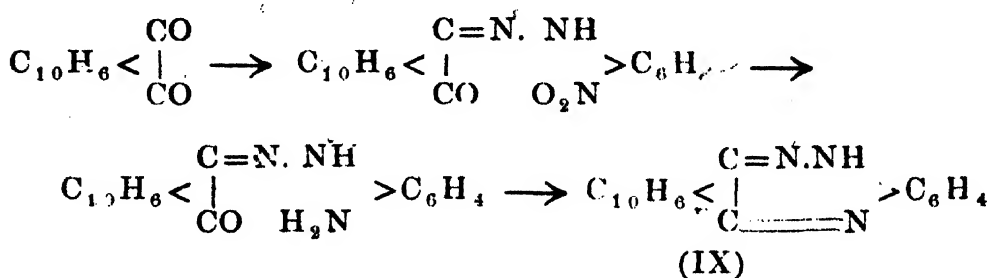
Benzil differs from the above diketones and forms only the dihydrazone which gets easily oxidised even on exposure to the air, forming diphenyl-dinitrodiphenyl-osotetrazine (?), thus:.

$$\begin{array}{l} Ph.\ C=N.\ NH.\ C_6H_4.\ NO_2 \\ \quad | \\ Ph.\ C=N.\ NH.\ C_6H_4.\ NO_2 \end{array} \quad \overset{O}{\longrightarrow} \quad \begin{array}{l} Ph.\ C=N.\ N.\ C_6H_4.\ NO_2 \\ \quad | \qquad | \\ Ph.\ C=N.\ N.\ C_6H_4.\ NO_2 \end{array}$$
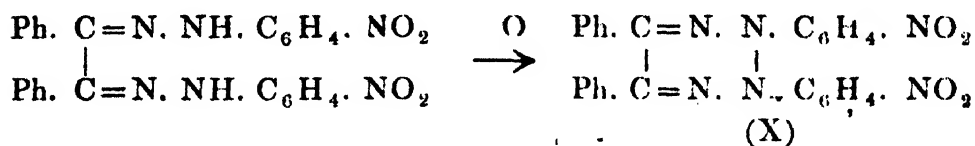
<div align="center">(X)</div>

(compare Pickel, *Annalen*, 232, 228).

o-Nitrophenylhydrazone of diacetyl monoxime loses one molecule of water when heated in a sealed tube at 100° with alcoholic hydrochloric acid to give 1-N-nitrophenyl-3 : 4-dimethyl-osotriazole, thus :

$$\begin{array}{l} CH_3.\ C=NOH \\ \quad | \\ CH_3.\ C=O \end{array} \longrightarrow \begin{array}{l} CH_3.\ C=NOH \\ \quad | \\ CH_3.\ C=N.\ NH.,C_6H_4.\ NO_2 \end{array}$$

$$\longrightarrow \begin{array}{l} CH_3.\ C=N \\ \quad | \qquad\quad > N.\ C_6H_4.\ NO_2 \\ CH_3.\ C=N \end{array}$$

<div align="center">(XI)</div>
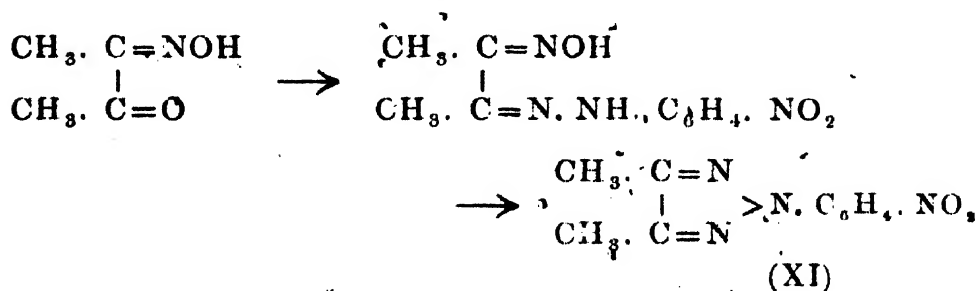
The resulting product is insoluble in alkali, showing the absence of any oxime grouping in it; moreover, it gives all

the reactions of an aromatic nitro group showing that the nitro group has not taken any part in this reaction (compare Willgerodt, *J. pr. Chem.*, 71, 404).

Oxalic ester readily forms oxalo-*o*-nitrophenylhydrazide (XII) which was expected to furnish an eleven-membered ring compound on reduction, thus :

$$CO.NH.NH.C_6H_4.NO_2 \atop CO.NH.NH.C_6H_4.NO_2 \quad (XII) \longrightarrow \quad CO.NH.NH.C_6H_4.NH_2 \atop CO.NH.NH.C_6H_4.NH_2$$

$$\longrightarrow \quad {CO.NH.NH.C_6H_4 \atop CO.NH.NH.C_4H_4}\!\!>\!NH$$
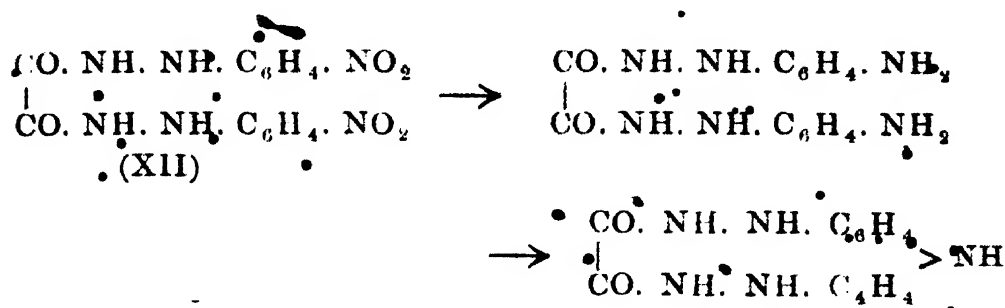
but that could not be isolated owing to the fact that it suffered decomposition at the time of concentrating the reduced solution (*vide* Experimental).

o-Phenylenediamine condenses with the nitrohydrazine with the elimination of one molecule of ammonia to form *o:o'*-nitroamino-hydrazobenzene, which in its turn loses another molecule of ammonia on reduction to form 2 : 3 : 6 : 7-dibenzo-4 : 5-dihydro-1 : 4 : 5-heptatriazine, thus :
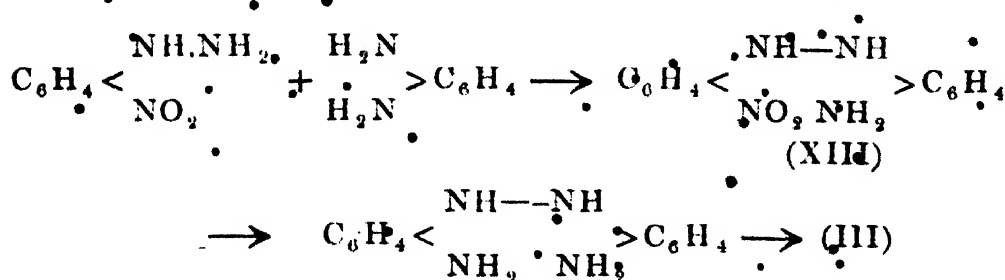
$$C_6H_4{<}{NH.NH_2 \atop NO_2} \;+\; {H_2N \atop H_2N}{>}C_6H_4 \longrightarrow C_6H_4{<}{NH-NH \atop NO_2\ NH_2}{>}C_6H_4 \atop (XIII)$$

$$\longrightarrow \quad C_6H_4{<}{NH-NH \atop NH_2\ NH_2}{>}C_6H_4 \longrightarrow (III)$$

EXPERIMENTAL.

2 : 3-Benzo-5 : 6-diphenyl-1 : 4 : 7-heptatriazine (I).

One gm. of benzil was allowed to react with 1 gm. of *o*-aminophenylhydrazine hydrochloride in 12 c.c. of glacial acetic acid in a sealed tube at 100° for 5·6 hours, when a crystalline solid substance was deposited. It was

thoroughly washed with water under suction pump" in order to make it free from the unreacted hydrochloride and was crystallised from acetone or pyridine as white needles melting at 114°. It becomes yellowish on exposure to air and dissolves in hydrochloric acid. (Found : N=14·24. $C_{20}H_{15}N_3$ requires N=14·14 per cent.).

Benzo-heptatriazine Compound with Alloxan.

One gm. of alloxan was allowed to react with 1 gm. of o-aminophenylhydrazine hydrochloride in 12 c.c. of absolute alcohol saturated with hydrogen chloride in a sealed tube at 100° for 4 to 5 hours when a yellow crystalline precipitate was found to have settled at the bottom of the tube. The precipitate was thoroughly washed with hot water and was found to be insoluble in all the ordinary organic solvents. It was dissolved in caustic soda, from which it was precipitated by the addition of hydrochloric acid as beautiful yellow crystalline plates, which did not melt even at 300°. (Found : N=30·77. $C_{10}H_7O_2N_5$ requires N=30·56 per cent.).

Benzo-heptatriazine Compound with Isatin.

It was prepared as the preceding compound and was crystallised from pyridine in shining red leaflets. It is fairly soluble in alcohol and acetone from which it does not crystallise well. It does not melt even at 300° and is insoluble both in acids and alkalis. (Found : N=24·1. $C_{14}H_{10}N_4$ requires N=23·93 per cent.).

2 : 3-Benzo-5 : 6-acenaphtha-1 : 4 : 7-heptatriazine.

A mixture of 1 gm. of the aminophenylhydrazine hydrochloride and 1 gm. of acenaphthenequinone was heated in a sealed tube with alcoholic hydrogen chloride as usual. The product crystallised from pyridine or

acetone in orange brown needles melting at 180°. It does not dissolve in alkali or in hydrochloric acid. (Found : N=15·82. $C_{18}H_{11}N_3$ requires N = 15·61 per cent.).

2 : 3-Benzo-5 : 6-phenanthra-1 : 4 : 7-heptatriazine.

The condensation was brought about as in the case of the above compounds. The product was at first crystallised from pyridine and then from acetone in white needles, melting at 220°. It is fairly soluble in alcohol but insoluble in ether, and chloroform. It dissolves with difficulty in strong hydrochloric acid. (Found : N = 14·35. $C_{20}H_{13}N_3$ requires N = 14·24 per cent.).

Phenanthra - o - phenylene - dihydrazone, similarly obtained from the hydrazine hydrochloride and phenanthraquinone monoxime, formed a green precipitate which was crystallised from pyridine in beautiful green needles. It is fairly soluble in alcohol, acetone and acids and melts at 160°. (Found : N = 18·2. $C_{20}N_{14}N_4$ requires N = 18·06 per cent.).

o-Amidophenylhydrazine and Isatine Monoxime: Formation of Isatin-orthophenylene-dihydrazone (II).

Equal parts of the reactants, in glacial acetic acid solution were heated in a sealed tube for 9 hours at 100°. The yellow needles, obtained on cooling, were repeatedly washed with water and finally crystallised from acetone. The compound is soluble in hydrochloric acid and melts at 270°. (Found : N = 28·35. $C_{14}H_{11}N_6$ requires N = 28·2 per cent.).

2 : 3 : 6 : 7-Dibenzo-4 : 5-dihydro-1 : 4 : 5-heptatriazine (III).

An intimate mixture of 1·5 gm. of the amino-phenylhydrazine hydrochloride and 1 gm. of o-phenylenediamine was heated on an oil-bath at 180-200°. Within the course of a few minutes a molten mass was obtained

nd ammonia began to evolve with the progress of the reaction. Heating was continued for about 5 hours when he evolution of ammonia ceased. The reaction product was finally powdered and boiled for about 10 minutes with water. The residue was dissolved in strong hydrochloric acid from which it was precipitated by alkali. This operation was repeated several times and finally it was purified from pyridine, m. p. about 300°. (Found : $N = 21.85$. $C_{12}H_{11}N_3$ requires $N = 21.32$ per cent.).

2 : 3-*Benzo*-6 : 7-*methylbenzo*-4 : 5-*dihydro*-1 : 4 : 5-*heptatriazine.*

This compound was prepared by heating an intimate mixture of o-aminophenylhydrazine hydrochloride and 1 gm. of 1 : 3 : 4-tolylenediamine at 180—200°. After extraction with hot water the residue was purified by dissolving in strong sulphuric acid and precipitating with a large quantity of water. This operation was repeated several times. It was crystallised from pyridine as a black crystalline powder. It is insoluble in almost all other organic solvents, m. p. above 300°. (Found : $N = 20.45$. $C_{13}H_{13}N_3$ requires $N = 19.89$ per cent.).

2 : 3-*Benzo*-6 : 7-*naphtho*-4 : 5-*dihydro*-1 : 4 : 5-*heptatriazine.*

It was prepared and purified by a similar method. It crystallised from pyridine in beautiful red crystals. It is insoluble in other organic solvents and melts at 146-48°. (Found : $N = 17.36$. $C_{16}H_{13}N_3$ requires $N = 17.0$ per cent.).

o-*Phenylene-semioxamazide* (IV).

One gm. of o-aminophenylhydrazine was gradually added to a nitrobenzene solution of 1 gm. of oxalyl chloride when the reaction commenced at once. To complete the reaction, the mixture was boiled for a few minutes. On concentration a brown precipitate came

out of the solution which was crystallised from nitro-benzene. It is insoluble in almost all other organic solvents, acids and alkalis and does not melt even at 300°. (Found : N$=24.15$. $C_8H_7O_2N_3$ requires N$=23.72$ per cent.).

o-Phenylene-semimalonamazide (V).

One gm. of o-aminophenylhydrazine hydrochloride, 2 gms. of sodium acetate and 1 gm. of malonic ester with a small quantity of absolute alcohol were heated in a sealed tube for 5-6 hours between 180 and 200°. The contents of the tube, after a thorough washing with water, were crystallised from pyridine in red plates which are insoluble in acids and alkalis, and do not melt even at 300°. (Found : N$=22.3$. $C_9H_9O_2N_3$ requires N$=21.98$ per cent.).

o-Phenylenethiocarbohydrazide (VIa).

An intimate mixture of 4 gms. of thiosemicarbazide and 2 gms. of the aminohydrazine hydrochloride was heated on an oil-bath at 180-200°, when ammonia evolved. The product was powdered, washed with hot water, dissolved in alkali and precipitated by the addition of dilute hydrochloric acid as a black precipitate which was insoluble in all ordinary organic solvents and did not melt even at 300°. (Found : N$=31.62$. $C_7H_9N_4S$ requires N$=31.1$ per cent.).

Disulphide.—An excess of iodine solution (in potassium iodide) was added drop by drop to the thio-compound dissolved just in the required quantity of sodium hydroxide solution, when a yellowish crystalline precipitate insoluble in all organic solvents and melting at 125° was obtained. (Found : N$=31.32$; S$=18.2$. $C_{14}H_{14}N_8S_2$ requires N$=31.28$; S$=17.9$ per cent.).

Acetaldehyde-o-nitrophenylhydrazone.

An alcoholic solution of 3 gms. of acetaldehyde was shaken with 1˙ gm. of o-nitrophenylhydrazine, when gradually orange-coloured needles came out of the solution. The product was crystallised from pyridine, m. p. 101°. It is insoluble in alcohol, acetone, ether and chloroform. (Found: N = 23˙52. $C_8H_9O_2N_3$ requires N = 23˙46 per cent.).

Reduction of the above Compound : Formation of μ-Methylbenziminazole.

Two gms. of the above hydrazone were heated with 6 gms. of granulated tin and 50 gms. of concentrated hydrochloric acid. After a few minutes, a clear red solution was obtained which, however, became colourless on further heating. The solution was then largely diluted with water and tin removed by sulphuretted hydrogen. The solution was then evaporated to dryness on the water-bath, the crystalline residue dissolved in the minimum quantity of water and the free base liberated by the addition of ammonia. It was crystallised from alcohol. It is soluble in ether and forms a soluble hydrochloride with hydrochloric acid and melts at 173°. (Found : N = 21˙30. $C_8H_8N_2$ requires N = 21˙21 per cent.).

o-Nitrobenzaldehyde-o-nitrophenylhydrazone.

A mixture of 2 gms. of o-nitrophenylhydrazine and 2 gms. of o-nitrobenzaldehyde in dilute alcoholic solution was heated under reflux for about 15 minutes, when an orange-coloured precipitate gradually formed in the solution. It was allowed to cool, filtered, washed with dilute hydrochloric acid and cold alcohol, and was crystallised from pyridine. It is insoluble in alcohol, ether, chloroform, alkalis and acids and melts at 223°. (Found : N = 19˙62. $C_{13}H_{10}O_4N_4$ requires N = 19˙58 per cent.).

Reduction of the above Hydrazone : Formation of 2 : 3 : 7 : 8-Dibenzo-1 : 5 : 6-octatriazine (VII).

The reduction of the above hydrazone was first tried with zinc dust and acetic acid and then with sodium hyposulphite (compare *J. Chem. Soc.,* 1923, *123,* 2408) but to no purpose. Finally, the action of tin and hydrochloric acid was tried with success. Three gms. of the above hydrazone were heated under reflux with tin and hydrochloric acid. After an hour, a pink-coloured clear solution was obtained which became colourless on further heating. After removing tin, the solution was evaporated to dryness and the crystalline hydrochloride thus obtained gave the free base on the addition of ammonia. It was crystallised from alcohol in shining colourless plates melting at 210°. (Found : N = 20·12. $C_{18}H_{11}N_3$ requires N = 20·09 per cent.).

Salicylaldehyde-o-nitrophenylhydrazone.

Two gms. of o-nitrophenylhydrazine were heated in alcoholic solution with 2 gms. of salicylaldehyde for about 30 minutes under reflux, when a bright red precipitate came out, which increased in quantity on cooling. It was filtered, washed with dilute hydrochloric acid, dissolved in cold sodium hydroxide solution, precipitated by hydrochloric acid and was then crystallised from pyridine. It is insoluble in water but soluble in alcohol and it melts at 192°. (Found : N = 16·48. $C_{13}H_{11}O_3N_3$ requires N = 16·3 per cent.).

2 : 3 : 7 : 8-Dibenzo-octa-1-oxy-5 : 6 diazine (VIII).

The method of preparation was the same as that of compound (VII). The hydrochloride crystallised from alcohol in white needles which melted at 145° with decomposition. (Found : N = 11·91. [$C_{13}H_{9}ON_2$] HCl requires N = 11·3 per cent.).

o-*Nitrophenylhydrazone* of *Acenaphthenequinone.*

A hot acetic acid solution of 1 gm. of the nitrohydrazine was added to a boiling acetic acid solution of 1·5 gm. of acenaphthenequinone when a red precipitate was formed. The mixture was boiled for some time under reflux, allowed to cool, filtered and the precipitate was finally crystallised from alcohol or pyridine in beautiful red crystals, which were insoluble in ether, chloroform, acids and alkalis and melted at 244°. (Found : N = 13·15. $C_{18}H_{11}O_3N_3$ requires N = 13·2 per cent.).

Reduction of the above Hydrazone : Formation of 2:3-Benzo-5:6-acenaphtha-1:4:7-hepta triazine (IX).

Two gms. of the above hydrazone were heated under reflux with 5 gms. of tin and 30 gms. of strong hydrochloric acid until an orange coloured clear solution was obtained. The solution on cooling gave crystals which were dissolved in the minimum quantity of water and the base precipitated by the addition of ammonia. It was crystallised from acetone in orange brown needles, m. p. 181°, which were found to be identical with the compound obtained by the action of o-aminophenylhydrazine on acenaphthenequinone. (Found : N = 15·85. $C_{18}H_{11}N_3$ requires N = 15·61 per cent.).

o-*Nitrophenylhydrazine and Anthraquinone :* *Formation of a Monohydrazone.*

A mixture of 1·5 gm. of anthraquinone, 1 gm. of the nitrohydrazine and 15 c. c. of alcohol was heated for 12 hours under reflux when a clear solution was obtained. A brownish red amorphous precipitate was formed when the reaction mixture was poured into water. It was filtered, washed with dilute hydrochloric acid, dried and finally crystallised from pyridine. It melted at 206-207°. It is soluble in alcohol but not in acids and alkalis.

(Found: $N = 12.5$. $C_{20}H_{13}O_3N_3$ requires $N = 12.24$ per cent.).

o-Nitrophenylmonohydrazone of a-Naphthaquinone.

One gm. of the nitrohydrazine was heated in alcoholic solution with 1 gm. of a-naphthaquinone for about 2 hours. Dark red crystals came out of the filtered solution on cooling, and a further quantity was obtained by pouring the reaction mixture in water. It is not soluble in any organic solvent excepting alcohol and even from that it could not be obtained in crystalline condition. It is soluble in strong sulphuric acid from which it can be precipitated by the addition of water. It is insoluble in alkali and in hydrochloric acid, and melts at 170°. The yield was about 1 gm. (Found: $N = 14.8$. $C_{16}H_{11}O_3N_3$ requires $N = 14.33$ per cent.).

o-Nitrophenylmonohydrazone of Phenanthraquinone.

One gm. of the nitrohydrazine and 1·5 gm. of phenanthraquinone were heated in acetic acid solution under reflux for about 15 minutes when an orange-red crystalline precipitate formed in the hot solution.. It was cooled and then filtered and the residue was crystallised from pyridine in beautiful red crystals melting at 245°. The yield was about 2 gms. It was insoluble in water and alcohol. (Found: $N = 12.32$. $C_{20}H_{13}O_3N_3$ requires $N = 12.24$ per cent.).

An Attempt to prepare o-Nitrophenyldihydrazone of Phenanthraquinone.

One gm. of the above hydrazone and 4 gms. of the nitro-hydrazine were heated in a sealed tube at 100° with 12 c. c. of absolute alcohol saturated with hydrogen chloride for 12 hours. The compound isolated from the reaction mixture melted at 245° and was proved to be the unconverted monohydrazone.

Benzil-o-nitrophenyldihydrazone.

A mixture of 1 gm. of the nitrohydrazine and 1·5 gm. of benzil was heated in acetic acid solution under reflux for an hour. The solution on standing for a few days yielded an orange red crystalline mass which was first crystallised from acetone and then from alcohol. It melted at 186° (Found: N = 17·55. $C_{26}H_{20}O_4N_6$ requires N = 17·5 per cent.).

Oxidation of the above Dihydrazone : Formation of
Diphenyl-dinitrodiphenyl-osotetrazine. (?)

The above dihydrazone was oxidised merely on exposure to the air to give a white amorphous powder. It was insoluble both in alcohol and acetone by which the unreacted dihydrazone was washed away, m. p. 200° with decomposition. (Found: N = 17·62. $C_{20}H_{18}O_4N_6$ requires N = 17·57 per cent.).

o-Nitrophenylhydrazone of Diacetylmonoxime.

One gm. of the nitrohydrazine was heated in dilute alcoholic solution with 0·7 gm. of diacetylmonoxime for about 2 hours under reflux. An orange red precipitate was formed on pouring the solution into water. It was dissolved in dilute caustic soda and, precipitated by dilute hydrochloric acid and was finally crystallised from pyridine. It is readily soluble in alcohol and in alkalis; m. p. 221-222°. (Found: N = 23·5. $C_{10}H_{12}O_3N_4$ requires N = 23·72 per cent.).

1-Nitrophenyl-3:4-dimethyl-1:2:5-osotriazole.

One gm. of the above hydrazone was heated in a sealed tube with 12 c. c. of absolute alcohol saturated with hydrogen chloride at 100° for 12 hours, when the colour of the solution suffered a gradual change. The brown solid mass, obtained from the contents of the tube, was filtered and crystallised from pyridine. It was insoluble both in acids and in alkalis, sparingly soluble in

alcohol and insoluble in ether. It melted at 285° with decomposition. It gave an azo colour with β-naphthol. after the nitro compound was reduced and diazotised. (Found: N = 25.77. $C_{10}H_{10}O_2N_4$ requires N = 25.68 per cent.).

Oxalo-*o*-nitrophenylhydrazide (XII).

A mixture of 1 gm. of oxalic ester and 1 gm. of *o*-nitrophenylhydrazine in glacial acetic acid solution was heated for half an hour under reflux when brick-red crystals were found to have deposited which, after filtration and washing, were crystallised from a large quantity of acetic acid; m. p. 265°. It is almost insoluble in all ordinary organic solvents. It dissolves in alkali producing a blue colouration. (Found: N = 23.38. $C_{14}H_{12}O_6N_6$ requires N = 23.33 per cent.).

Reduction of the above Compound.

One gram of the hydrazide was heated with 6 gms. of tin and 50 c. c. of concentrated hydrochloric acid: Within an hour, the hydrazide went into solution producing a beautiful pink colouration which was discharged on further heating. Tin was removed from the solution by sulphuretted hydrogen and the filtrate was evaporated to dryness on the water-bath and the residue was found to be a tarry product.[1]

o-Nitrophenylhydrazine and *o*-Phenylenediamine: Formation of o : o′-Nitroaminohydrazobenzene (XIII).

An intimate mixture of 1.5 gm. of *o*-phenylenediamine and 1 gm. of *o*-nitrophenylhydrazine was heated

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[1] It is expected that if the evaporation is carried on at a lower temperature under reduced pressure then this sort of decomposition can be avoided. But, unfortunately, the experiment could not be repeated for want of a sufficient quantity of *o*-nitrophenylhydrazine.

up to 100°. The whole mass fused and the reaction was allowed to proceed until the evolution of ammonia ceased. The product was ground to a fine powder and boiled with water. The residue was dissolved in dilute hydrochloric acid and precipitated by alkali. This operation was repeated several times. Finally an attempt was made to crystallise it from pyridine but no crystals came out of the solution. It dissolves in acids producing a beautiful red fluorescence and does not melt even at 300°. (Found: N = 23·38. $C_{12}H_{12}N_4O_2$ requires N = 22·9 per cent.).

Reduction of the above Compound: Formation of 2 : 3 : 6 : 7 :-Dibenzo-4 : 5-dihydro-1 : 4 : 5-heptatriazine (IV).

The reduction was carried out in the same way as that of acetaldehyde-*o*-nitrophenylhydrazine. The brown amorphous base was finally crystallised from pyridine, m. p. above 300°. (Found: N = 21·8. $C_{12}H_{11}N_3$ requires N = 21·32 per cent.). The compound is apparently identical with that obtained by the interaction of *o*-aminophenylhydrazine and *o*-phenylenediamine (*vide* p. 49).

The work is in progress.

Our thanks are due to Sir P. C. Rây and Dr. J. C. Ghosh for the kind interest they have taken in the work.

The Ionisation Potential of Hydrogen Fluoride.

BY

A. N. KAPPANNA.

The ionisation potentials of hydrochloric, hydrobromic and hydriodic acids have been determined experimentally by Foote and Mohler (HCl only, *J. Am. Chem. Soc.*, 1920, 42, 1882) and Franck and Knipping (*Zeit. Physik*, 1921, 7, 328). The experimental difficulties involved in a direct determination of the ionisation potential of hydrofluoric acid are obvious. It is therefore of some interest to calculate this value indirectly. Two attempts have so far been made in this direction. Turner (*Phil. Mag.*, 1924, 48, 1010), on the basis of a linear relationship which he found to exist between the atomic numbers and the quantum defects computed from the ionisation potentials of the hydrogen halide molecules, calculated the ionisation potential of HF to be 17.9 ± 0.5 volts. More recently Glockler (*Phil. Mag.*, 1925, 50, 997) has calculated this value from thermochemical considerations based on the value obtained by Grimm and Herzfeld (*Zeit. Physik*, 1923, 19, 141) for the difference between the heat of dissociation of the fluorine molecule (D_F) and the electron affinity (E_F) of the fluorine atom and finds it to be 15.67 ± 0.7 volts. Again, obtaining D_F and E_F by extrapolating the known values for the other halogens and obtaining an independent value for ($D_F - E_F$), the ionisation potential was found to come out to be 15 volts. The values obtained by these two
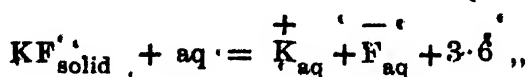
authors are very much higher than those for other hydrogen halides which lie close to one another.

$$
\begin{array}{lll}
\text{HI} & \dots & 12\cdot6 \text{ volts}^{1} \\
\text{HBr} & \dots & 13\cdot0 \text{ ,,} \\
\text{HCl} & \dots & 13\cdot59 \text{ ,,}
\end{array}
$$

Glockler considers that a certain amount of uncertainty exists about the values of D_F and E_F which he used in his calculations. A value lower than that of Glockler has been obtained below from calculations made from a slightly different standpoint from that of Glockler, the thermochemical data made use of being of a more certain nature.
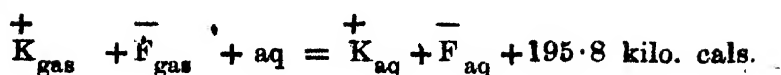
Fajans (*Ber. Deut. Phys. Ges.*, 1919, *21*, 549) in extending the work of Börn on lattice energies pointed out that the heat of solution of a solid salt may be regarded as the sum of two effects, *viz.*, (1) the heat required to convert the solid salt into free gas ions, or what is the same as lattice energy and (2) the heat of solution of these gas ions.

Potassium fluoride and potassium chloride have the same lattice structure as rock salt. According to the calculations of Fajans and Herzfeld (*Zeit. Physik*, 1920, *2*, 309) the lattice energies for potassium fluoride and chloride are 192·2 and 159·0 kilo. cals respectively. The heats of solution of KF and KCl are $+3\cdot6$ and $-4\cdot4$ respectively (Landolt and Börnstein's *Tables*). Expressed in equation form—

$$
\overset{+}{K}_{gas} + \overset{-}{F}_{gas} = KF_{solid} + 192\cdot2 \text{ kilo. cals}
$$

$$
KF_{solid} + aq = \overset{+}{K}_{aq} + \overset{-}{F}_{aq} + 3\cdot6 \text{ ,,}
$$

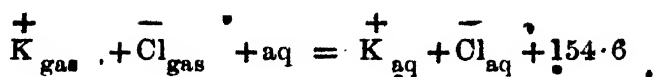[1] These values are taken from Franck (*Zeit. Physik*, 1922, *11*, 160).

Adding

$$\overset{+}{K}_{gas} + \overset{-}{F}_{gas} + aq = \overset{+}{K}_{aq} + \overset{-}{F}_{aq} + 195 \cdot 8 \text{ kilo. cals.}$$

Similarly,

$$\overset{+}{K}_{gas} + \overset{-}{Cl}_{gas} + aq = \overset{+}{K}_{aq} + \overset{-}{Cl}_{aq} + 154 \cdot 6$$

or,

$$(\overset{-}{K}_{gas} + aq) - (\overset{-}{Cl}_{gas} + aq) = \overset{-}{F}_{aq} - \overset{-}{Cl}_{aq} + 41 \cdot 2 \text{ kilo. cals...(1)}$$

Again,

$$HCl_{gas} + aq = \overset{+}{H}_{aq} + \overset{-}{Cl}_{aq} - 17 \cdot 43 \text{ k. cals (Landolt's } Tables \text{).;}$$

$$\overset{+}{H}_{gas} + \overset{-}{Cl}_{gas} = HCl_{gas} + 313 \text{ k. cals (from ionisation}$$
$$\text{potential).}$$
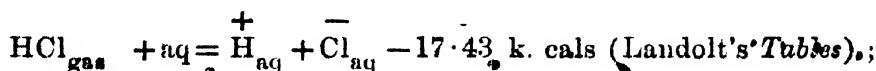
Adding

$$\overset{+}{H}_{gas} + \overset{-}{Cl}_{gas} + aq = \overset{+}{H}_{aq} + \overset{-}{Cl}_{aq} + 295 \cdot 57 \text{ k. cals} \quad \therefore \quad (2)$$
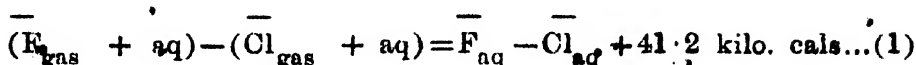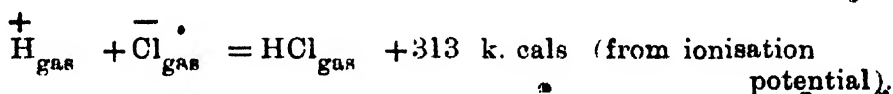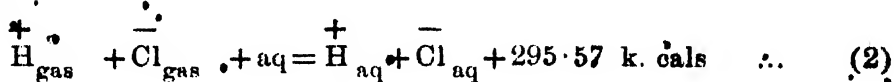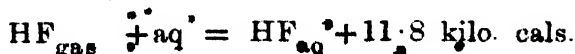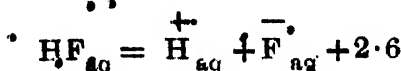
The solution of hydrofluoric acid is quite different from that of strong acids. Very little of HF is found to be ionised in solution and when its neutralisation is effected by strong alkalis, the amount of heat evolved is $2 \cdot 6$ k. cals greater than in the case of the other halogen hydrides. Here if we assume that HF exists in solution practically as non-ionised, we can regard this excess of heat of neutralisation as the heat liberated in the process of the ionisation of the acid.
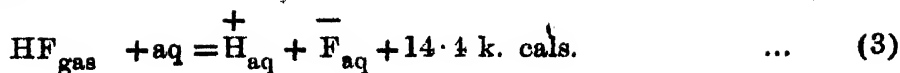
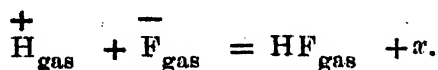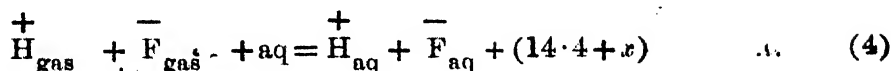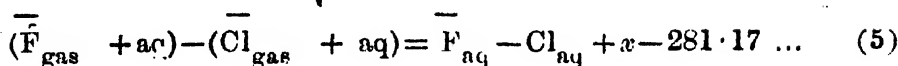Guntz (*Compt. rend.*, 1883, *96*, 1659) found the heat of solution of HF to be $11 \cdot 8$ k. cals.

$$HF_{gas} + aq = HF_{aq} + 11 \cdot 8 \text{ kilo. cals.}$$

and

$$HF_{aq} = \overset{+}{H}_{aq} + \overset{-}{F}_{aq} + 2 \cdot 6$$

Adding

$$HF_{gas} + aq = \overset{+}{H}_{aq} + \overset{-}{F}_{aq} + 14 \cdot 4 \text{ k. cals.} \qquad \ldots \quad (3)$$

If x be the ionisation energy of HF_{gas} in heat units,

$$\overset{+}{H}_{gas} + \overset{-}{F}_{gas} = HF_{gas} + x.$$

Combining this with equation (3), we get

$$\overset{+}{H}_{gas} + \overset{-}{F}_{gas} + aq = \overset{+}{H}_{aq} + \overset{-}{F}_{aq} + (14 \cdot 4 + x) \qquad \ldots \quad (4)$$

Now, subtracting (2) from (4), we have

$$(\overset{-}{F}_{gas} + aq) - (\overset{-}{Cl}_{gas} + aq) = \overset{-}{F}_{aq} - Cl_{aq} + x - 281 \cdot 17 \ldots \quad (5)$$

Equations (1) and (5) are identical. Thus we find

$$x - 281 \cdot 17 - 41 \cdot 2 = 0$$

or,

$$x = 622 \cdot 87 \text{ k. cals.}$$

Expressed in volts

V (the ionisation potential of HF) $= 14 \cdot 02$

The assumption made above that HF exists in solution practically as non-ionised is only approximately correct; so that this introduces a small error in the value of x we have arrived at. But this error would be very small when expressed in volts. It will be seen that the value obtained in this calculation is only 0·5 volts higher than the ionisation potential of HCl.

My best thanks are due to Dr. J. C. Ghosh for his kind encouragement.

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The Relation between the Surface Tension and Vapour Pressure of Binary Mixtures.

By

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It is a well known fact that the curve, representing the relation between vapour pressure and composition usually belongs to one of three main types:—

(a) The vapour pressures of the mixture may lie between those of the pure components.

(b) The vapour pressure curve may have a maximum.

(c) The vapour pressure curve may have a minimum.

It was expected that the surface tension of binary mixtures would also give similar types of curves and in order to determine the exact relationship between surface tensions and vapour pressures, the present investigation was undertaken.

Moreover attempts have been made by Volkmann and Whatmough and others to obtain suitable formulæ for calculating the surface tensions of mixtures. Volkmann (*Ann. Physik*, *188*, [iii], 320) suggested that the surface tension of binary mixtures can be represented by the formula,—

$$\gamma = \gamma_1 v_1 + \gamma_2 v_2$$

where γ represents the surface tension of the mixture, γ_1 and γ_2 represent the surface tension of the components, v_1 and v_2 volumes of the liquids taken fractionally. This formula has got many exceptions. Later on Whatmough (*Zeit. physikal. Chem.*, 1902, *39*, 158) modified the above formula and took into account the volume changes which

take place on mixing and proposed the following for-
mula :—

$$\gamma = R(\gamma_1 v_1 + \gamma_2 v_2)$$

where γ, γ_1, γ_2, v_1, v_2 have the same significance as before
and R is the ratio of the calculated to the observed
density.   By the help of the data obtained as the result
of the present investigation, the validity of the above-
mentioned formulae was tested by comparing the observed
values with the values calculated.

Experimental.

Zawidski (*Zeit. physikal. Chem.*, 1900, *35*, 129) has
determined the vapour pressure of a large number of
binary mixtures and from his work the following mix-
tures, belonging to each of the three characteristic types,
were selected for the present investigation.

1.   Mixtures, the vapour pressure curves of which
correspond with a straight line.
  (*a*) Benzene and ethylene dichloride.
  (*b*) Ethylene dibromide and propylene dibromide.
  (*c*) Bromobenzene and toluene.
  (*d*) Chlorobenzene and toluene.

2.   Mixtures, the vapour pressure curves of which
pass through a minimum.
  (*a*) Acetic acid and pyridine.
  (*b*) Chloroform and acetone.
  (*c*) Methyl alcohol and ethyl iodide.

3.   Mixtures, the vapour pressure curves of which
pass through a maximum.
  (*a*) Ethyl iodide and ethyl acetate.
  (*b*) Carbon tetrachloride and ethyl acetate.
  (*c*) Carbon disulphide and acetone.
  (*d*) Carbon tetrachloride and ethyl iodide.

Purification of the Chemicals.

The chemicals were all purified by the usual methods. In case of pyridine, however, the sample boiling between 112°—116° was taken. Although this happens to be impure, yet reference to the work of Zawidski (*loc. cit.*) will show that the same sample was used by him in connection with his work on vapour pressure.

The method used for the determination of surface tension was the sphere detachment method due to Ferguson (*Phil. Mag.*, 26, 926).

Both Volkmann's and Whatmough's formulæ were used for obtaining values of surface tension by calculation but as Whatmough's formula was not found to show any decided advantage over Volkmann's formula, in the following tables calculated values in accordance with Volkmann's formula are only given.

Benzene and Ethylene Dichloride.

Vol. % Ethylene bromide.	γ at 17°		γ at 50°	
	Obs.	Cal.	Obs.	Cal.
0	29·17	...	24·08	...
10	29·33	29·42	24·38	24·38
20	29·50	29·67	24·66	24·67
30	29·61	29·92	24·98	24·99
50	30·05	30·42	25·56	25·56
70	30·53	30·93	26·16	26·16
90	31·21	31·42	26·75	26·75
100	31·68		27·35	

2. *Propylene Dibromide and Ethylene Dibromide.*

Vol. % Propylene dibromide.	γ at 17°		γ at 40°		γ at 85°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	38·42	...	35·28	...	32·25	...
10	38·02	38·17	34·81	34·98	31·88	31·86
20	37·68	37·91	34·48	34·67	31·47	31·48
30	37·35	37·66	34·02	34·39	31·09	31·09
40	37·01	37·39	33·60	34·10	30·71	30·70
50	36·45	37·15	33·38	33·81	30·31	30·31
60	36·35	36·90	33·18	33·53	29·93	29·93
70	36·22	36·65	33·01	33·24	29·51	29·54
80	35·94	36·40	32·67	32·95	29·15	29·15
90	35·88	36·14	32·52	32·67	28·77	28·77
100	35·88		32·38		28·38	

3. *Bromobenzene and Toluene.*

Vol. % Bromobenzene.	γ at 20°		γ at 35°		γ at 50°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	25·15	...	23·16	...	22·43	...
10	26·11	25·86	23·74	24·03	23·49	23·36
20	27·19	26·57	25·18	24·90	24·30	24·29
30	28·10	27·28	26·05	25·77	25·21	25·22
40	28·65	27·99	26·81	26·64	26·23	26·15
50	28·90	28·71	27·66	27·51	27·77	27·09
60	29·03	29·41	28·55	28·37	28·20	28·02
70	30·15	30·13	29·52	29·24	29·03	28·95
80	31·38	30·84	30·45	30·11	29·91	29·88
90	31·98	31·55	30·89	30·98	30·77	30·81
100	32·26	...	31·85	...	31·74	...

4. Chlorobenzene and Toluene.

Vol. % Chlorobenzene.	γ at 20°		γ at 35°		γ at 50°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	25·15	...	23·16	...	22·43	...
10	25·40	25·67	23·51	23·68	23·15	23·17
20	25·52	26·19	24·23	24·56	23·97	23·91
30	26·09	26·77	25·02	25·26	24·77	24·66
40	26·24	27·25	25·62	25·98	25·44	25·39
50	26·90	27·77	26·63	26·66	25·95	26·15
60	27·88	28·29	27·38	27·36	26·81	26·88
70	28·31	28·82	27·94	28·06	27·71	27·62
80	28·78	29·34	28·62	28·76	28·43	28·37
90	29·60	29·87	29·21	29·42	29·16	29·11
100	30·39	...	30·16	...	29·85	...

The observed and calculated values coincide very well in all these cases; hence we can say that when vapour pressures of mixtures obey the mixture law, the surface tensions of those mixtures also obey the mixture law, and when these values are plotted graphically, we get a straight line.

5.   Acetic Acid and Pyridine.

Vol. % Acetic acid.	γ at 20°		γ at 40°		γ at 80°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	37·22	...	34·32	...	28·32	...
10	36·52	36·17	34·27	33·36	28·32	27·57
20	36·02	35·12	33·71	32·61	28·31	26·82
30	35·20	34·08	33·01	31·45	28·08	26·02
40	34·58	33·01	33·67	30·49	28·02	25·31
50	33·95	31·96	32·15	29·53	27·78	24·56
60	33·08	30·91	31·45	28·58	27·37	23·81
70	32·15	29·86	30·65	27·62	26·79	23·05
80	31·68	28·81	29·61	26·61	25·37	22·30
90	29·68	27·75	27·49	25·71	23·52	21·55
100	26·71	...	24·75	...	20·89	...

6.   Chloroform and Acetone.

Vol. % Acetone.	γ at 15°		γ at 25°		γ at 35°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	27·29	...	25·67	...	24·92	...
10	27·05	26·92	25·56	25·34	24·81	24·54
20	26·78	26·56	25·43	25·01	24·65	24·16
30	26·48	26·19	25·25	24·68	24·48	23·30
40	26·18	25·85	25·06	24·35	24·18	23·40
50	25·88	25·45	24·81	23·92	23·92	23·02
60	25·45	25·09	24·58	23·69	23·61	22·67
70	25·15	24·72	24·24	23·36	23·29	22·26
80	24·66	24·35	23·75	23·03	22·83	21·88
90	24·17	23·99	23·18	22·69	22·07	21·50
100	23·62	...	22·37	...	21·18	...

7. *Methyl Alcohol and Ethyl Iodide.*

Vol. % Ethyl iodide.	γ at 25·2°		γ at 37·5°		γ at 45°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	19·65	...	18·97	...	18·46	...
10	20·75	20·72	20·04	19·93	19·49	19·29
20	23·66	21·79	22·90	20·89	21·81	20·13
30	25·12	22·87	23·81	21·86	22·95	20·97
40	26·04	23·95	24·62	22·82	23·60	21·80
50	26·89	25·02	24·83	23·78	24·23	22·64
60	27·03	26·09	26·02	24·75	24·81	23·74
70	28·21	27·17	26·78	25·71	25·34	24·31
80	28·98	28·24	27·46	26·67	25·82	25·14
90	29·61	29·32	28·18	27·64	26·37	25·97
100	30·39	...	28·60	...	26·91	...

In this case also we find that the observed values
of surface tension are greater than those calculated while
the vapour pressures are less than those calculated and
the curve passes through maxima.

8. *Carbon Tetrachloride and Ethyl Acetate.*

Vol. % Ethyl acetate.	γ at 15°		γ at 35°		γ at 50°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	26·58	...	25·02	...	23·10	...
10	26·01	26·27	23·85	24·59	21·48	22·16
20	25·53	25·96	22·95	24·16	20·51	22·22
30	25·13	25·66	22·31	23·74	19·82	21·78
40	24·87	25·39	22·05	23·31	19·54	21·34
50	24·55	25·05	21·75	22·88	19·35	20·90
60	24·31	24·74	21·58	22·45	19·19	20·45
70	24·11	24·44	21·29	22·02	19·04	20·00
80	23·89	24·33	21·07	21·60	18·91	19·58
90	23·72	23·82	20·88	21·77	18·81	19·14
100	23·56	...	20·74	...	18·70	...

9. *Ethyl Acetate and Ethyl Iodide.*

Vol. % Ethyl acetate.	γ at 18°		γ at 35°		γ at 50°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal
0	31·06	...	28·74	...	26·68	...
10	29·39	30·27	26·51	27·94	24·58	25·88
20	28·22	29·49	25·41	27·13	23·08	25·08
30	27·21	28·70	24·42	26·33	22·08	24·29
40	26·41	27·91	23·78	25·52	21·41	23·49
50	25·82	27·12	23·16	24·72	20·82	22·69
60	25·18	26·34	22·56	23·92	20·74	21·89
70	24·58	25·55	21·96	23·11	19·78	21·09
80	24·10	24·76	21·40	22·31	19·08	20·30
90	23·68	23·98	20·98	21·50	19·01	19·50
100	23·19	...	20·70	...	18·70	...

10.   *Ethyl Iodide and Carbon Tetrachloride.*

Vol. % Ethyl iodide.	γ at 25·2°		γ at 37·5°		γ at 50°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	28·05	...	26·54	...	24·72	...
10	28·21	28·28	26·55	26·75	24·82	24·93
20	28·24	28·52	26·60	26·95	25·01	25·14
30	28·39	28·75	26·76	27·16	25·14	25·35
40	28·62	28·99	27·05	27·36	25·36	25·56
50	29·06	29·22	27·40	27·57	25·61	25·72
60	29·35	29·45	27·62	27·78	25·84	25·97
70	29·60	29·69	27·85	27·98	26·11	26·18
80	29·81	29·92	28·10	28·19	26·38	26·39
90	30·13	30·16	28·31	28·39	26·62	26·70
100	30·39	...	28·60	...	26·81	...

11.   *Acetone and Carbon Disulphide.*

% Acetone.	γ at 15°		γ at 25°		γ at 35°	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	23·06	...	21·62	...	21·17	...
10	23·64	24·09	22·28	22·69	21·89	22·19
20	24·69	25·13	23·20	23·76	22·16	23·21
30	24·88	26·17	24·38	24·84	23·38	24·23
40	25·58	27·20	24·74	25·91	24·12	25·25
50	26·58	28·24	25·20	26·98	25·02	26·27
60	27·33	29·27	26·03	27·99	25·82	27·29
70	28·32	30·31	27·02	29·12	26·86	28·32
80	29·64	31·24	28·36	30·19	28·07	29·34
90	31·70	32·38	29·93	31·27	29·17	30·36
100	33·41	...	32·24	...	31·38	...

2.

Here we find that the observed values are much less than those calculated by Volkmann's formula and we sum up by saying that when the vapour pressure values of a mixture are greater than those calculated, the surface tension ones are less than those calculated, and thus when these values are plotted graphically the curve will pass through minima.

Summary.

This investigation was undertaken with a view to find out a relation between surface tension and vapour pressure of binary mixtures and to see whether the mixtures, the vapour pressure curves of which show maxima, minima or straight lines, would behave similarly with respect to surface tension or not. Moreover it was tried to determine how far Volkmann's and Whatmough's formulæ were applicable for calculating the surface tension of mixtures. As a result of the present investigation the following results have been arrived at:—

1. When the vapour pressure curve is a straight line, the surface tension one is also a straight line.

2. When the vapour pressure curve shows a maximum, the surface tension one shows a minimum.

3. When the vapour pressure curve shows a minimum, the surface tension one shows a maximum.

4. Volkmann's formula was found applicable in case of those mixtures, the vapour pressure and surface tension of which are straight lines.

5. Whatmough's formula was not found to show any decided advantage over Volkmann's formula.

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On Triethylene Trisulphide, and 1:4-Dithian

BY

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AND

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Triethylene trisulphide and its derivatives have already been described by one of us (*J. Chem. Soc.*, 1920, **117**, 1090; *ibid*, 1922, *121*, 1279). Bennet and Berry (*J. Chem. Soc.*, 1925, *127*, 910) have recently prepared this cyclic polysulphide and conclude that the so-called trisulphide is in reality 1:4-dithian.

In view of this divergence in views we have recently re-investigated the subject and we find that the compounds prepared by our method as also by V. Meyer's method are identical in properties. A molecular weight determination in benzene solution gave the value 119·5, that required by the formula $(C_2H_4)_2S_2$ being 120. Bennet and Berry determined the molecular weight in nitrobenzene solution.

There are, however, substantial grounds for adhering to the formula previously proposed. It has been already hinted at that in certain cases this complex sulphide parts with the group C_2H_4S and is converted into the simpler modification (*loc. cit.*, 1280), in other words, the one form can easily pass into the other. Moreover, the formation of the two distinct platinum derivatives $(C_2H_4)_3S_2PtCl_3$ and $(C_2H_4)_3S_3PtCl_4$ cannot be accounted for except on the assumption that in certain cases polymerisation does take place,[1] thus:

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[1] The substance depolymerises in the gaseous state as well as in dilute solution; the vapour density of the substance was measured by Hoffmann's method, and it conformed approximately to the formula $(C_2H_4)_2S_2$ (*cf.* $2O_3 \rightleftarrows 3O_2$).

$$3(C_2H_4)_2S_2 \longrightarrow 2(C_2H_4)_3S_3$$
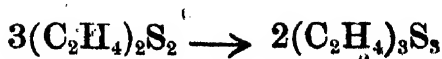
It has lately been found that when the dithian is treated with an aqueous instead of an alcoholic solution of chloroplatinic acid, the compound of the formula $(C_2H_4)_3S_2PtCl_3$ is *invariably* obtained. Its formation justifies the use of the formula $(C_2H_4)_3S_3$ for the sulphide in question; the dropping off of an atom of sulphur has already been noticed when a sulphide is loaded with a heavy molecule like platinic chloride (*loc. cit.*, 1279; *cf.* also Mann and Pope, *J. Chem. Soc.*, 1923, *123*, 1179). Dithian $(C_2H_4)_2S_2$ cannot be expected to yield a compound containing three ethylene radicles—in fact, these platinum compounds are crucial instances in support of our view.

EXPERIMENTAL.

Resublimed dithian (m. p. 113°) was heated with an aqueous solution of platinic chloride and continuously 'teased' with a rod. A yellow crystalline compound was formed. It was drained on filter paper washed with water, dried and then washed with boiling benzene to remove traces of dithian that might be present. The preparation was repeated several times. (Found: Pt = 43·68, 43·52, 43·26, 43·44; Cl = 24·25; S = 14·58; C = 15·33; H = 2·23. $(C_2H_4)_3S_2PtCl_3$ requires Pt = 43·63; Cl = 23·59; S = 14·17; C = 15·94; H = 2·66 per cent.)

As compounds of this type have been known to contain alcohol or ether of crystallisation (this *Journal*, 1924, *1*. 70; foot-note), care was taken not to use alcohol or ether in the preparation, because discrimination between $(C_2H_4)_3S_2PtCl_3$ and $(C_2H_4)_2S_2PtCl_3$, EtOH by analysis is difficult.

Lengthened Chain Compounds of Sulphur.

BY

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AND

KSHITISH CHANDRA BOSE-RÁY.

Recently, we had occasion to prepare 1 : 4-dithian in quantity by the method described by V. Meyer (*Ber.*, 1886, *19*, 3263), namely, by the interaction of dithioethylene glycol and ethylene bromide in presence of sodium ethylate, thus :

$$C_2H_4(SNa)_2 + C_2H_4Br_2 = 2NaBr + C_2H_4 <^S_S> C_2H_4$$
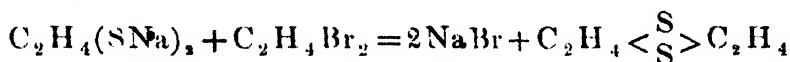
According to Meyer the reaction can be so regulated at will that either dithian alone or its polymer will be the product. If a small quantity of alcohol be poured over the sodium mercaptide and the requisite amount of ethylene bromide added all at once without cooling, the polymer is formed with evolution of heat. If, however, fifty times the weight of alcohol be used as diluent and the ethylene bromide be added drop by drop under cooling, the volatile and readily soluble dithian is the sole product. The polymer, when boiled several hours with phenol, is changed into the simpler form.

We have subjected the "polymer" obtained according to the first method to a systematic examination, and have found it to be a mixture of two brominated compounds, one of which had the formula $BrC_2H_4(SC_2H_4)_{48}Br$—a fact which apparently escaped the notice of Meyer. In one instance a dibromide of the formula $BrC_2H_4(S \cdot C_2H_4)_{40} \cdot Br$ was also obtained. The reaction appears to be sensitive, so that very slight changes in experimental conditions produce variations in the results obtained.

An attempt to determine the molecular weight of the compound $BrC_2H_4(SC_2H_4)_{48}Br$ by its dissolution in ethylene bromide by the ebullioscopic method gave very interesting results. The molecular weight found was about half that required by theory. It was discovered that the apparent anomaly was due to the splitting up of the long-chain dibromide by continued boiling with ethylene bromide according to the following scheme :

$$BrC_2H_4(SC_2H_4)_{48}Br + C_2H_4Br_2 = 2BrC_2H_4(SC_2H_4)_{24}Br$$
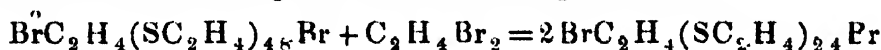
The slight deviation from the theoretical molecular weight is easily accounted for by the fact that simultaneously a much simpler compound of formula $BrC_2H_4(S\cdot C_2H_4)_{12}\cdot Br$ is formed in small quantities by the further break-up of the resulting molecule, thus :

$$BrC_2H_4(SC_2H_4)_{24}Br + C_2H_4Br_2 = 2BrC_2H_4(SC_2H_4)_{12}Br$$

The above reaction was also studied under slightly modified conditions, namely, with an excess of ethylene bromide. When the latter was added all at once without cooling, three distinct compounds were obtained in three different preparations. They had the formulæ (i) $BrC_2H_4(SC_2H_4)_{26}\cdot Br$, (ii) $BrC_2H_4(SC_2H_4)_{32}Br$, and (iii) $BrC_2H_4(SC_2H_4)_{48}Br$ respectively. Compound (i) was obtained when comparatively small quantities of the reactants were used, while (ii) and (iii) were products when larger quantities of the reactants were employed. If the temperature of the reaction is higher, a larger number of molecules coalesce to form the new compound. This explanation receives support from the fact that when the reaction of Meyer modified as above was carried out according to the second method, that is, with cooling, much simpler compounds of formulæ $BrC_2H_4(SC_2H_4)_{18}Br$ and $BrC_2H_4(SC_2H_4)_{10}Br$ respectively were obtained. It will be noticed, however, that prolonged boiling with ethylene bromide again disintegrates the compound into simpler molecules (vide supra). If these brominated compounds are heated at about 10° higher

than their melting points they decompose into dithian and simpler brominated compounds. That the "polymer" described by V. Meyer is not a mere polymeride of dithian is further corroborated by the fact that some compounds obtained by Bennet (*J. Chem. Soc.;* 1922, *121,* 2144).which appeared to be polymerides of dithian behave differently from Meyer's so-called " polymer " when heated with phenol.

In all the methods employed dithian was formed in very considerable quantities. In fact, it was always the main product of reaction.

The course of the formation of the brominated derivatives may be represented thus :

$$BrC_2H_4 \boxed{Br + Na} \quad S. C_2H_4. S \boxed{Na + Br} \quad C_2H_4.Br + \ldots\ldots$$

$$\ldots\ldots + NaS \cdot C_2H_4 \cdot S \boxed{Na + Br} . C_2H_4.Br.$$

$$= BrC_2H_4 \cdot (S \cdot C_2H_4)_n Br + nNaBr.$$
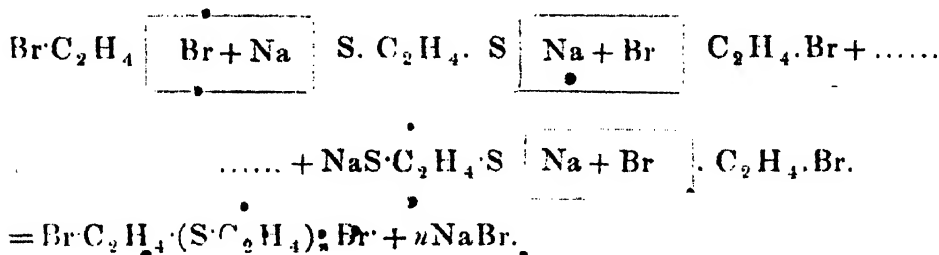
This explains the fact that the product *invariably* contains $(n+1)$ C_2H_4 residues and n sulphur atoms, where n is an even integer.

EXPERIMENTAL.

V. Meyer's Method.—One g. of sodium, dissolved in 25 c.c. of alcohol, was added to 2 gms. of dithioethylene glycol and finally at the ordinary temperature all at once 4 g. of ethylene bromide were poured over it. A white amorphous solid mass immediately separated out with great evolution of heat. The product was filtered under suction and washed twice with cold benzene in which dithian is excessively soluble. The filtrate on evaporation yielded an abundant crop of dithian. The residue, insoluble in benzene, was then washed with alcohol and then several times with water and finally triturated in a mortar with water so as to remove the last traces of

sodium bromide. The dried residue was extracted with boiling benzene; the filtrate on cooling gave a very small quantity of a product which could not be obtained sufficiently pure for analysis. The insoluble residue dissolved completely in hot nitrobenzene. The filtrate on cooling deposited a white mass of m. p. 170° which when examined under the microscope proved to be amorphous. (Found : $Br = 5·96$; $S = 49·95$. $BrC_2H_4(SC_2H_4)_{40}Br$ requires $Br = 6·18$; $S = 49·45$ per cent.). This preparation was repeated with double the quantities of the reactants and the products separated as above. The compound which was thrown down from nitrobenzene had the m. p. 163°. It dissolved also in molten naphthalene from which it separated out in a crystalline form having the same m. p. (Found: $Br = 5·30$; $S = 51·76$; $C = 37·76$; $H = 6·87$. $BrC_2H_4(SC_2H_4)_{48}Br$ requires $Br = 5·21$; $S = 50·06$; $C = 38·33$ and $H = 6·39$ per cent.). This preparation was repeated several times with identical results.

The above compound was found to be soluble in hot ethylene bromide and an attempt was made to determine its molecular weight by the ebullioscopic method. (Found : M. W. $= 1486$. Calc., M. W. $= 3068$). The ethylene bromide solution on cooling gave a product which was filtered and washed with ethylene bromide and alcohol. Its m. p. was 147°. (Found : $S = 49·01$; $Br = 10·87$. $ErC_2H_4(SC_2H_4)_{24}·Br$ requires $S = 47·17$; $Br = 9·83$ per cent.) The calculated M. W. of the compound is 1628 which fairly agrees with the observed value. The slight deviation is due, no doubt, to the presence of a very small quantity of a simpler compound (m. p. 100°), which is precipitated from the mother-liquor by alcohol. (Found : $S = 44·65$; $Br = 17·99$. $Br·C_2H_4·(S·C_2H_4)_{12}·Br$ requires $S = 42·29$; $Br = 17·62$ per cent.)

The procedure described above was slightly modified as follows :

(*i*) Sodium (2·8 g.), dissolved in 80 c.c. of alcohol, was treated with 5·64 g. dithioethylene glycol, the flask being immersed in ice. Ethylene bromide (17·28 g.) was then run in drop by drop with constant shaking. The resulting solid mass was washed with alcohol, benzene, and ether and finally with water several times to remove sodium bromide completely. The benzene filtrate on evaporation gave a copious yield of dithian. The insoluble residue was extracted with boiling benzene. The filtrate on cooling deposited an amorphous white solid, m. p. 120° (Found: Br=20·46; S=40·86. $BrC_2H_4 \cdot (SC_2H_4)_{10} \cdot Br$ requires Br=20·31; S=43·61 per cent.). The insoluble product was dissolved in hot nitrobenzene from which on cooling a compound of m. p. 162° was precipitated. (Found: Br=14·71; S=46·02. $BrC_2H_4 \cdot (SC_2H_4)_{16}Br$ requires Br=13·93; S=44·6 per cent.).

(*ii*) To 1·38 g. sodium, dissolved in 20 c.c. alcohol, were added 2·82 g. dithioethylene glycol. Ethylene bromide (8·64 g.) was then added all at once. Heat was developed and a white mass separated, which was filtered, washed with alcohol and then with cold benzene and finally with water. The benzene extract contained a considerable quantity of dithian. The dried residue was treated with boiling benzene. The filtrate on cooling gave a product which shrinks at 122° and melts at 130°. It was, however, obtained in too small a quantity to admit of analysis. The benzene-insoluble mass was taken up with boiling nitrobenzene which on cooling gave a white compound. It shrinks at 145° and melts at 155°. (Found: Br=9·14, 9·31; S=48·55; C=37·48; H=6·30. $BrC_2H_4(SC_2H_4)_{26}Br$ requires Br=9·1; S=47·59; C=37·07; H=6·18 per cent.) This reaction was repeated with four times the weights of the reactants and the products separated as above. In one preparation the product from nitrobenzene had the m. p. ·157—59°.

(Found : Br=7·96, ·7·86 ; S=49·76. BrC₂H₄(SC₂H₄)₃₂·
Br requires Br=7·60 ; S=48·58 per cent.) In
another preparation 'a compound of' m. p. 163° was
·isolated. (Found : Br=5·18 ; S=51·90: BrC₂H₄(SC₂H₄)₄₈
Br requires Br=5··21 ; S=50·06 per cent.) The com-
pound is, therefore, identical with that 'of the same
m. p., obtained by Meyer's method.

Transformation of the Long-chain Sulphides into 1 : 4-
Dithian by Heat.—The sulphides were kept melted in a
test-tube at about 10° above their respective m. p.'s for
a few hours. A sublimate (long, transparent needles)
was slowly deposited in the cooler part of the tube. It
melted at 113° and a mixture of this substance and 1:4-
dithian did not depress the m. p. ; obviously the product
is 1 : 4-dithian.

Summary and Conclusion.

From the foregoing investigation it is evident that

(*i*) The main product of interaction of dithiothylene
glycol and ethylene bromide is 1 : 4-dithian.

(*ii*) V. Meyer's so-called "polymer" of dithian is a
mixture of brominated long-chain derivatives, amongst
which the compound Br·C₂H₄·(S·C₂H₄)₄₈·Br is almost always
formed under the conditions stated above. This appears
to be ·the "first instance of a crystalline organic sulphur
compound of such high molecular weight as 3068.

(*iii*) Whenever any of these compounds is kept heated
for several hours above their m. p.'s, dithian (the main
product of decomposition) sublimes off and brominated
compounds are left behind. In fact, it is not necessary
to heat them with phenol for this purpose.

UNIVERSITY COLLEGE OF SCIENCE
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On the Stability of Colloidal Solutions.

Part V.

The Effect of similarly charged Ions as a Factor in Electrolyte Antagonism in the Coagulation of Sols and the Mechanism of Stabilisation.

BY

KSHITISH CHANDRA SEN.

In several previous papers (Sen and Mehrotra, *Zeit. anorg. Chem.*, 1925, *142*, 345 ; Sen, *J. Phys. Chem.*, 1925, 29, 517 ; *Zeit. anorg. Chem.*, 1925, *149*, 139) the antagonistic effect of electrolytes on the coagulation of sols has been investigated and some general conclusions have been reached.

It should be stated here that in explaining the so-called cationic antagonism in the cases studied by him, Weiser (*J. Phys. Chem.*, 1924, 28, 232) advanced the view that the antagonistic action of two cations is only observed when they have greatly different precipitating powers. This mistake was undoubtedly due to the fact that he never used suitable mixtures of univalent cations as the coagulating ions. A similar fact was also simultaneously observed by Mukherjee and Ghosh (this *Journal*, 1924, *1*, 213) who suggested that a slight adsorption of anions would explain the observed antagonism of the several pairs of electrolytes. Similarly in the case of positively charged sols, the writer has shown the existence of antagonistic effects of suitable mixture of salts. In the present paper the earlier experiments with copper ferrocyanide sol have been extended with mixtures of univalent cations as the coagulating ions and an interesting effect of the influence of dilution of the

sol on the antagonistic action of salt pairs has been pointed out. The method of experimentation with the sols has been the same as described in previous papers.

TABLE I.

Sol—Copper ferrocyanide ; *Electrolytes*—$K_2C_2O_4$ + NaCl.

$N/2$ $K_2C_2O_4$ taken in c.c.	$N/2$ NaCl reqd. for coagulation		Difference.
	Observed.	Calculated.	
0	1·35	...	...
0·2	1·50	1·246	0·254
0·5	1·55	1·091	0·459
0·8	1·40	0·885	0·515
1·0	1·30	0·831	0·469
1·5	0·95	0·572	0·378
2·0	0·60	0·312	0·288
2·6	0·0	...	...

TABLE II.

Sol—Copper ferrocyanide : *Electrolytes*—Potassium tartrate + NaCl.

$N/2$ Potassium tartrate taken in c.c.	$N/2$ NaCl reqd. for coagulation.		Difference.
	Observed.	Calculated.	
0	1·35	...	...
0·2	1·45	1·19	0·26
0·5	1·35	0·95	0·40
0·8	1·05	0·71	0·34
1·0	0·85	0·55	0·30
1·3	0·50	0·31	0·19
1·7	0·0	...	...

TABLE III.

Sol—Copper ferrocyanide: *Electrolytes*—Na$_2$C$_2$O$_4$ + KCl.

N/3 Na$_2$C$_2$O$_4$ taken in c.c.	N/2·20 KCl reqd. for coagulation.		Difference.
	Observed.	Calculated.	
0·0	1·3	...	...
0·5	1·6	1·134	0·466
1·0	1·55	0·967	0·583
1·5	1·30	0·801	0·499
2·0	1·10	0·634	0·466
2·5	0·80	0·468	0·332
3·9	0·0	...	...

These results at first sight might indicate that the antagonism is between sodium and potassium ions, but the following results will show that the antagonistic behaviour is really due to the effect of the anions (*cf.* Mukherjee and Ghosh, *loc. cit.*).

TABLE IV.

Sol—Copper ferrocyanide: *Electrolytes*—Potassium tartrate + KCl

N/2 Potassium tartrate taken in c.c.	N/2·02 KCl reqd. for coagulation.		Difference.
	Observed	Calculated	
0·0	1·3	...	...
0·2	1·3	1·15	0·15
0·5	1·0	0·92	0·08
0·8	0·75	0·69	0·06
1·0	0·60	0·54	0·06
1·8	0·35	0·31	0·04
1·7	0·0	...	...

TABLE V.

Sol—Copper ferrocyanide: *Electrolytes*—$K_2C_2O_4 + KCl$

N/2 $K_2C_2O_4$ taken in c.c.	N/2·02 KCl reqd. for coagulation.		Difference.
	Observed.	Calculated.	
0·0	1·3	...	...
0·1	1·5	1·25	0·25
0·2	1·6	1·20	0·40
0·3	1·65	1·15	0·50
0·4	1·63	1·10	0·53
0·5	1·55	1·05	0·50
0·6	1·46	1·00	0·46
0·8	1·30	0·90	0·40
1·0	1·15	0·80	0·35
1·2	0·98	0·70	0·28
1·8	0·55	0·40	0·15
2·0	0·40	0·30	0·10
2·2	0·28	0·20	0·08
2·4	0·13	0·10	0·03
2·6	0·0	...	...

It may be observed that the antagonistic action is slightly more pronounced when the coagulating ions are different. This is probably due to the fact that the introduction of 'the same ion depresses the ionisation of stabilising electrolytes, potassium oxalate and tartrate. It seems probable that the stabilising effect is due to the oxalate and tartrate ions which is supported by the fact that these acids have not such a great effect as the corresponding salts, though the effect of hydrogen ion

has also to be remembered. These results thus show that the antagonistic effect of some salt pairs is due to the presence of anions. In a previous paper (*J. Phys. Chem.*, 1925, 29, 517), it was shown that ferrocyanide, ferricyanide, oxalate, tartrate, etc., Ions have considerable peptising effect on copper ferrocyanide sol and the difference in the precipitating values of these salts from that of potassium chloride is mainly due to this fact. It has now been observed that mixtures containing potassium chloride and either potassium ferrocyanide or oxalate or citrate or potassium tartrate show an antagonistic behaviour with copper ferrocyanide sol. Further, potassium oxalate has a higher precipitation value than potassium tartrate on copper ferrocyanide sol which points to the fact that the oxalate ion has a greater effect than the tartrate ion. Quite parallel to this, potassium oxalate and potassium chloride mixture shows a much greater antagonistic effect than a mixture of potassium chloride and potassium tartrate. These results, therefore, establish the fact that the presence of similarly charged ions can produce antagonistic effects in the case of mixtures of salts having the same coagulating ion.

In carrying these coagulation experiments, it has been found that the concentration of the sol has a great effect on the observed antagonistic action of mixtures of electrolytes. It is well known that several colloids like arsenious sulphide, require higher concentrations of univalent electrolytes of the type KCl for coagulation when diluted than when concentrated, and an explanation was given on the assumption that similarly charged ion has a greater effect on a diluted sol than on a concentrated sol. If this be the case, then the antagonistic action of a pair of electrolyte, say, KCl and BaCl$_2$, would be more pronounced on a diluted sol of arsenious sulphide than on a concentrated sol. The following data

show that this anticipation has been realised (*cf. Zeit. anorg. Chem.*, 1925, *149*, 139).

TABLE VI.

Sol—Arsenious sulphide: *Electrolytes*—KCl + BaCl$_2$

M/2 KCl taken in c.c.	Difference in the observed and calculated values of BaCl$_2$ M/200 reqd. for coagulation.	
	Original sol 3·4 gm./litre.	$\frac{1}{2}$ diluted sol
0·3	0·76	0·86
0·5	0·90	1·0
0·8	0·89	0·96
1·0	0·70	0·80
1·2	0·51	0·64

As to the mechanism of the stabilising effect of the similarly charged ion, it is apparent that the stability reaches a maximum and then decreases with the gradual addition of the stabilising electrolyte.

If we assume that for small additions of the stabilising electrolyte the preferential adsorption of similarly charged ion increases proportionately, then the log curve for the amount of electrolyte added and the difference between the observed and the calculated values of the coagulating electrolyte which gives a measure of the stability of the colloid system, should be a straight line. This happens to be the case with such electrolytes as FeCl$_3$+KCl, Al(NO)$_3$+KCl, etc., on a positively charged sol of ferric hydroxide, as has been pointed out by Ghosh and Dhar (*J. Phys. Chem.*, 1925, *29*, 659) who have also shown some limitations of this reasoning in a later paper

(private communication). Unfortunately, however, a correct idea of these curves cannot be obtained unless a large number of points are taken on both sides of the maximum. No suitable experimental data for this are obtainable in the literature, though some can be obtained by interpolation. For this reason a large number of data have been obtained with the mixture $K_2C_2O_4 + KCl$ and given in Table V. In the following table, data on the coagulation of arsenious sulphide sol are also tabulated.

TABLE VII.

Sol—Arsenious sulphide : *Electrolytes*—NaCl+CaCl$_2$

M/2 NaCl taken in c.c.	Difference in the observed and calculated values of CaCl$_2$ M/200 reqd. for agulation.
0·1	0·26
0·2	0·49
0·3	0·67
0·4	0·79
0·5	0·86
0·6	0·89
0·7	0·90
0·8	0·88
0·9	0·83
1·0	0·72
1·1	0·66
1·2	0·56
1·3	0·48
1·4	0·39

The log curves of the results given in Tables V and VII are plotted in the following figure. It will be observed
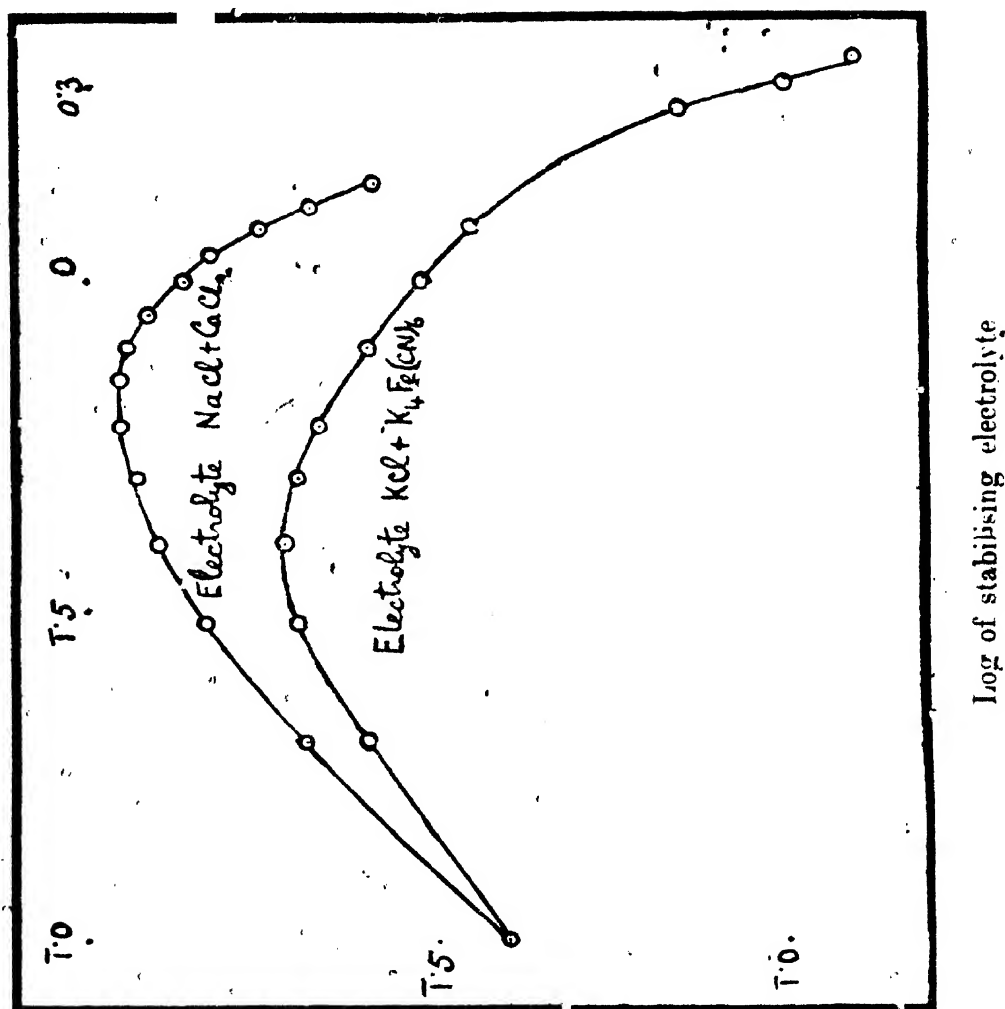
Log of difference

that the first three points in the curve for the mixture $K_2C_2O_4 + KCl$ can be represented by a straight line. After the maximum point, however, the relations are no longer simple owing to the fact that the adsorption of the *same* charged ion does not increase proportionately any more with the addition of the stabilising electrolyte. On the other hand, the adsorption of the coagulating ion may be assumed to be proportional to the amount of the stabilising electrolyte at the end of the curve, and consequently

the last few points give an approximate straight line. In the case of the mixture $NaCl + CaCl_2$ it will be apparent that the phenomena is more complicated and this is certainly due to the fact that the preferential adsorption of Cl' by arsenious sulphide sol is never so marked as is observed in the case of say, adsorption of $Fe^{...}$ ion by ferric hydroxide sol. For this reason it cannot be assumed that the increase in the amount of adsorption of Cl' ions by arsenious sulphide is connected with the amount of KCl added in such a simple manner as is the case of adsorption of the same charged ions by ferric hydroxide sol as estimated from the data of Freundlich and Wosnessensky. (*Kolloid Zeil.*, 1923, *33*, 222; *cf.* Ghosh and Dhar, *loc. cit.*). Consequently it seems that in the study of antagonistic action of electrolytes much importance cannot be given to these logarithmic interpretations of the experimental data for the reasons given above (*cf.* Clowes, *J. Phys. Chem.*, 1916, *20*, 407) and also because of the fact that the so-called exponential equations do not give us any real knowledge about the true mechanism of the process (Fischer, *Trans. Faraday Soc.*, 1922, *17*, 805).

Summary.

(1) It has been shown that mixtures of potassium oxalate and potassium chloride, and potassium tartrate and potassium chloride show antagonistic behaviour in the coagulation of copper ferrocyanide sol. Similar effects are also observed with mixtures of potassium chloride and potassium citrate, ferrocyanide, etc.

(2) It has been observed that mixtures containing the same stabilising ion but different univalent coagulating ions show a greater antagonistic behaviour than mixtures containing the same coagulating ion. This may be due to

the depression of ionisation of the stabilising electrolyte by the addition of a same ion of the electrolyte.

(3) It has been pointed out that the antagonistic effect of two electrolytes is more pronounced with a diluted sol than with a concentrated sol of arsenious sulphide. A similar effect will probably be obtained with other sols which behave in dilution experiments like arsenious sulphide.

(4) The mechanism of stabilisation in presence of two electrolytes is briefly discussed.

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The Action of Organic Compounds on Sodium Hydrogen Sulphate

BY

HORACE BARRATT, DUNNICLIFF AND SUCHDEV SINGH.

The treatment of trisodium hydrogen disulphate or sodium sesquisulphate, $Na_3H(SO_4)_2$ with successive quantities of 99·95 per cent. ethyl alcohol has been shown to cause a small but progressive fall in acidity in the solid residues. After leaving the salt in contact with separate quantities of alcohol for six consecutive days the acidity fell from 18·64 to 17·75 per cent. H_2SO_4 (total fall=0·89 per cent.). The efforts of Butler and Dunnicliff (*J. Chem. Soc.*, 1920, *117*, 649) to make a continuous extraction were unsuccessful. This continuous extraction has now been carried out under reduced pressure in a Soxhlet and bumping entirely prevented by bubbling through the alcohol in the flask, a slow stream of specially dried air by means of a capillary tube. The pressure was so adjusted that the alcohol boiled at 45°C. Extractions were carried out from 8-10 hours daily and the salt was allowed to remain under alcohol overnight.

Acidity on successive days in ether dried samples: 18·66; 18·64; 18·61; 18·59; 18·56; 18·51; 18·50; 18·47; 18·48% H_2SO_4 (total fall after nine days, 0·18% H_2SO_4).

Crystalline $Na_3H(SO_4)_2$, obtained by the fractional crystallisation of a solution of sodium hydrogen sulphate in water, is also unattacked by alcohol or ether and it has been shown (*loc. cit.*) that the sesquisulphate is a definite compound and not a mixture of the normal and hydrogen sulphate.

The corresponding hydrogen sulphate of ammonium, $(NH_4)_3H(SO_4)_2$ behaves in a similar manner (Dunnicliff, *J. Chem. Soc.*, 1923, *123*, 476).

These results demonstrate the remarkable stability of the sesquisulphates of sodium and ammonium to alcohol, a property which has been utilised in developing an analytical method (Dunnicliff, *ibid*, 1923, *123*, 731).

The fact that, while ordinary dry sodium hydrogen sulphate is unattacked by ether, two-thirds of its sulphuric acid is extracted by alcohol, suggests a formula for the dry solid salt, at least three times the empirical formula, *i.e.*, $(NaHSO_4)_3$. The formula should show that the sulphuric acid extractable by alcohol is in a different state of combination from that which is not.

The hydrogen sulphates may be divided into three classes :—

(*a*)   Those from which the whole of the sulphuric acid is extracted by ether-alcohol or ether : lithium (silver, barium, strontium, etc.).

(*b*)   Those in which two-thirds of the sulphuric acid is extracted by alcohol but which are not attacked by ether : sodium, ammonium.

(*c*)   Those which are not attacked by ether-alcohol or ether : potassium, rubidium, caesium.

In order to distinguish between these three states of combination, the following formulae are proposed.

Class (a).
$$\left(\begin{array}{c} RO \\ RO \end{array} > SO_2 \right), \quad \begin{array}{c} HO \\ HO \end{array} > SO_2$$
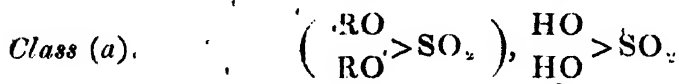
or as a co-ordination compound

$$\left[\begin{array}{c} RO \\ RO \end{array} > S < \begin{array}{c} OH \\ OH \end{array} \right] SO_4$$
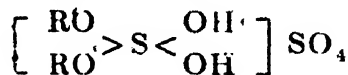
and would include compounds of classes (*b*) and (*c*) when associated with more sulphuric acid

Class (b)
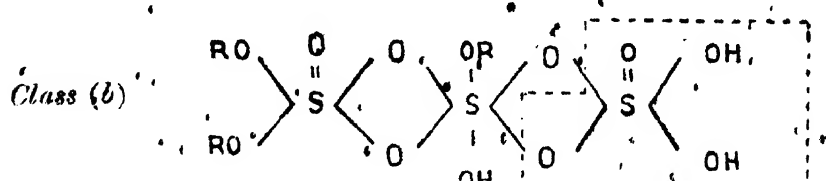
The sulphuric acid extractable by alcohol is shown in dotted area. An asymmetric formula is proposed because the extraction of the solid salt appears to take place without solution. The formula of the sesqui salt would then become

$$\begin{array}{ccc} & O & O \\ RO & \| & O & \| & OR \\ RO & {>}S{<}{O}{>}S{<} & OH \end{array}$$
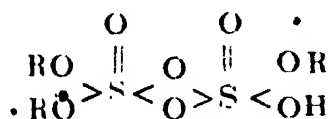
not $R_2SO_4, RHSO_4$ a formula which would imply that the $RHSO_4$ part of the molecule could be attacked by alcohol to which $R_3H(SO_4)_2$ is inert. The formation of the sesquisulphate from a symmetrical formula would necessitate either solution or intramolecular change and neither of these suggestions appears to be feasible.

Class (*c*).—The ordinary formula is suggested

$$\begin{array}{c} RO \\ {>}SO_2 \\ HO \end{array}$$
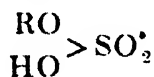
(Lowry, *Inorganic Chemistry*, 1923, pp. 160 and 353).

Hence, the stability of the hydrogen sulphates to alcohol and ether increases progressively with increase in the atomic weight of the alkali metal in the salt. It is interesting to note that compounds of classes (*a*) and (*b*) are deliquescent at ordinary humidities while those of class (*c*) and the sesquisulphates of sodium and ammonium are not. Since sulphuric acid is hygroscopic it suggests that this property in acid sulphates may be associated with a sulphur atom combined with two hydroxy groups as shown in the formulae proposed. A remarkable feature of these results is the sudden manner in which this property changes.

The amorphous form of sodium sesquisulphate obtained by the action of alcohol on sodium hydrogen sulphate has chemical properties identical with those exhibited by the crystalline variety of the same

compound obtained by the fractional crystallisation of an aqueous solution of sodium hydrogen sulphate.

It is contended that sodium hydrogen sulphate cannot be described as " soluble " in alcohol' since it has not been found possible to obtain any alcoholic extract of sodium hydrogen sulphate in which sodium sulphate and sulphuric acid are present in stoichiometric proportions. Alcohol does not dissolve sodium hydrogen sulphate—it decomposes it.

Hydrogen sulphates of sodium formed 'from' sodium sulphate and sulphuric acid, and containing more than $40\cdot83$ per cent. of sulphuric acid, are acted on by ether yielding the hydrogen sulphate having the empirical formula, $NaHSO_4$.

A systematic examination of the system Na_2SO_4-H_2SO_4-C_2H_6O has recently been carried out by Dunnicliff and his co-workers. The equilibrium has been studied (a) by the action of alcohol on sodium hydrogen sulphate and (b) by the action of alcoholic sulphuric acids on sodium hydrogen sulphate and, while experiments on the limited range attackable by method (a) have presented no great difficulty, those carried out by method (b) have been complicated by the peptisation of the solid phase and sometimes the entire contents of the tube solidified into a firm jelly. By a physico-chemical method it has been shown that the solid phases in contact with alcoholic sulphuric acids having concentrations between 20 and 40 per cent. H_2SO_4 have an acidity of about 41%, corresponding with sodium hydrogen sulphate, $NaHSO_4$.

In view of the statement that ordinary sodium hydrogen sulphate is stable to continuous extraction with ether, the results in Tables V and VI (*J. Chem. Soc.*, 1920, *117*, 658, 659) obtained by the extraction of the " mush " with ether show that the extractability of sulphuric acid from sodium hydrogen sulphate by ether

depends upon the physical state of the substance. Thus, in the gelatinous state, in which a large surface is exposed to the liquid, ether slowly extracts sulphuric acid while in the powdered state the amount of sulphuric acid removed is negligible over the same interval of time (maximum time investigated = 3 weeks' extraction in each case).

It has been found that many other organic compounds extract sulphuric acid from sodium hydrogen sulphate. Experiment with methyl, ethyl, *n*-propyl, *iso*-propyl, butyl, primary *iso*-butyl and *iso*-amyl alcohols show that the weight of alcohol required to reduce the acidity of a given weight of sodium hydrogen sulphate to about 18·70 per cent. increases with the weight of the alkyl group in combination with the hydroxyl.

Table I shows this relationship and it is remarkable that up to the butyl alcohols the molecular proportions of alcohol to hydrogen sulphate are about the same throughout.

TABLE I.

Action of Aliphatic Saturated Alcohols on Sodium Hydrogen Sulphate.

Alcohol.	B. p. at 790 mm. (Lahore).	$\dfrac{\text{Wt. of alcohol}}{\text{Wt. of NaHSO}_4}$	Approx. molec. proportions of C_2H_6O to NaHSO$_4$	Acidity of residue after ether extraction.
CH_3OH	63·5	3·5	15·1:1	18·72
C_2H_6OH	78·1	5·5	14·4:1	18·69
$C_3H_8OH(n)$	95·5	7·4	14·8:1	18·68
$C_3H_7OH(iso)$	80·5	7·6	15·2:1	18·67
$C_4H_9OH(n)$	116·0	9·0	14·6:1	18·79
$C_4H_9OH(iso$-primary).	109·0	9·1	14·6:1	18·69
$C_6H_{11}OH(iso$-butyl carbinol).	129·5	26·1	35·4:1	18·68

Benzyl alcohol alone extracts acid from the salt but equal parts of benzyl alcohol and ether cause a very small fall in acidity.

Ethyl aceto-acetate extracts acid slowly.

Borneol dissolved in ether extracted some acid from the salt.

The hydroxy compounds, phenol, hydroquinone, resorcinol, dissolved in ether, were without action on sodium hydrogen sulphate.

Action of Ketones.

Acetone, b. p. 55·8°C.

Acetone : NaHSO$_4$ :: 7 : 1. Residual acidity of solid 27·44—27·48%. The residue was treated with more acetone ; residual acidity 18·62%. Acetone : NaHSO$_4$ :: 10 : 1 Residual acidity of solid, 18·61—18·68%. The liquid phase changed colour on standing and, after three weeks, was dark brown and viscous owing to secondary changes between the extracted sulphuric acid and the acetone.

Methyl ethyl ketone, b. p. 79·5°C.

Ketone : NaHSO$_4$ :: 7 : 1 ; time of interaction 20 hours.

Acidity of residue, 35·31 per cent.

Ketone : residue :: 5 : 1 ; further treatment overnight.

Acidity of residue, 20·36 per cent.

Two further extractions gave 19·90 and 18·64 per cent. respectively.

Acetophenone, b. p. 199—200°C.

Ketone : NaHSO$_4$ :: 11 : 1 (interaction 2½ hours).

Acidity of residue, 35·33 per cent.

Benzophenone, m. p. 47·6°C.

Ketone : NaHSO$_4$ :: 7·3 parts to 10 parts : 1.

The ketone was dissolved in a weight of ether about 14 to 15 times the weight of sodium hydrogen sulphate taken. Fall in acidity negligible.

Similar experiments performed on benzoquinone and camphor dissolved in excess of ether gave a negligible fall in acidity.

Pyridine and quinoline combine with the hydrogen sulphate to form gelatinous substances.

It is observed that, for an extraction by ketones, $CH_3CO.X$ to a corresponding degree, the greater the group X, the larger the ratio $\dfrac{\text{weight of ketone}}{\text{weight of hydrogen sulphate}}$ becomes.

Hence though, for a given alcohol or ketone, the amount of decomposition is dependent on the variations the above ratio, it is clear that for different alcohols and ketones, the solid phase developed in contact with a given organic liquid is dependent on some factor other than the concentration of the acid in the organic liquid.

From the above results it appears that compounds which contain a primary or secondary alcoholic group or ketones in which there is one methyl group interact with sodium hydrogen sulphate and extract sulphuric acid.

An interesting point arises. Since alcohol reacts with sodium hydrogen sulphate, can it act catalytically? Thus : a small quantity of alcohol is dissolved in a considerable quantity of ether. Sodium hydrogen sulphate is treated with such a quantity of the mixture, that if $\frac{2}{3}$rds of the sulphuric acid were extracted from the hydrogen sulphate presented to it, the solution would still have a concentration of sulphuric acid within the limits of the concentration of sulphuric acid in alcohol which are in equilibrium with the intermediate sulphate $Na_3H(SO_4)_2$. This would suggest that the sulphuric acid is extracted by the alcohol which then hands it over to the ether, this process being continued until the concentration of the sulphuric acid in the mixed solvents passes beyond the limits of the existence of the intermediate

sulphate. (This was not possible owing to the amount of alcohol-ether mixture used.) Experiments give no support to this theory in the case of either alcohol or acetone. The amount of acid extracted decreases as the concentration of alcohol or acetone diminishes. This decrease in extraction was also observed in the case of benzyl alcohol.

TABLE II.

Action of Mixtures of Ethyl Alcohol and Ether on Sodium Hydrogen Sulphate.

Wt. of alcohol. / Wt. of ether.	Wt. of mixture used per g. of sodium hydrogen sulphate.	Acid extractable 0·272 g. Acid actually extracted.	Acidity of solid residue % H_2SO_4.
1 : 4·57	4·78	0·1787	27·90
1 : 9·10	6·94	0·1729	28·43
1 : 18·2	7·60	0·0972	34·42
1 : 36·4	6·77	0·0823	35·50

TABLE III.

Action of Mixtures of Acetone and Ether on Sodium Hydrogen Sulphate.

Wt. of acetone. / Wt. of ether.	Wt. of mixture used per g. of sodium hydrogen sulphate.	Acid extractable 0·272 g. Acid actually extracted.	Acidity of solid residue % H_2SO_4.
1:1	10	0·0850	35·30
1·2:1	11	0·0966	34·47
1·4:1	12	0·1739	28·34
1·6:1	13	0·1740	28·33
1·8:1	14	0·1760	28·16
2·0:1	15	0·1754	28·23

The last three results are roughly of the order of the residual acidity when 7 parts of pure acetone react with 1 of NaHSO₄.

The frequency with which solids having acidities of about 35 and 28 per cent. acidity are developed is remarkable.

It is suggested that the reaction is due to the ionisation of the alcohol or the ' enol ' form developed or present in such ketones as react and which are limited to these containing the CH_3CO group. The action of the ether appears to decrease the ionisation of alcohols and the "enolisation" of ketones since the specific conductivities of alcohol and acetone are progressively decreased by increasing quantities of ether. The determinations given in Tables IV and VI were made on the material actually used in the experiments on sodium hydrogen sulphate.

It will be observed that, though the specific conductivity of acetone is greater than that of alcohol, its ability to extract sulphuric acid from sodium hydrogen sulphate is much smaller.

Specific Conductivities of Mixtures of two Organic Liquids.

TABLE IV.

Alcohol and Acetone.

Percentage of acetone in the mixture.	Specific conductivities.
0	$2 \cdot 29 \times 10^{-6}$ mhos
20	$3 \cdot 06 \times 10^{-6}$,,
40	$3 \cdot 73 \times 10^{-6}$,,
60	$4 \cdot 35 \times 10^{-6}$,,
80	$5 \cdot 04 \times 10^{-6}$,,
100	$5 \cdot 28 \times 10^{-6}$,,

TABLE V.

Alcohol and Ether.

Percentage of alcohol in the mixture.	Specific conductivities.
100	$22 \cdot 9 \times 10^{-7}$ mhos
80	$14 \cdot 3 \times 10^{-7}$,,
60	$12 \cdot 3 \times 10^{-7}$,,
40	$6 \cdot 6 \times 10^{-7}$,,
20	$0 \cdot 86 \times 10^{-7}$,,
0	$0 \cdot 19 \times 10^{-7}$,,

TABLE VI.

Acetone and Ether.

Percentage of acetone in the mixture.	Specific conductivities.
100	$52 \cdot 8 \times 10^{-7}$ mhos
80	$31 \cdot 8 \times 10^{-7}$,,
60	$15 \cdot 6 \times 10^{-7}$,,
40	$3 \cdot 8 \times 10^{-7}$,,
20	$0 \cdot 34 \times 10^{-7}$,,
0	$0 \cdot 19 \times 10^{-7}$,,

So far, the attempts to find an adequate chemical interpretation (intermediate compound formation) or physico-chemical explanation of these results have been unsuccessful.

The authors desire to thank Dr. Mata Prasad for his help in the determination of the specific conductivities of the mixed liquids.

The Use of Leucotrope as a Benzylating Agent.

By

HLA BAW.

Leucotrope (phenylbenzyldimethyl ammonium chloride) has been used for some time commercially as a benzylating agent (*cf.* D. R. P. 184381 and ·281543). Tschugaeff· and Chlopin (*Ber.*, 1914, *47*, 1272) used it for the preparation of dibenzyl telluride. In the present paper an account is given of its application to the benzylation of phenols and also of a similar application of *para-*. and *meta*-nitroleucotropes; the nitroleucotropes have already been applied in the production of the nitrobenzyl ethers of cellulose (Peacock, *Indian Patent*, Appn. No. 11548 of 1925).

Leucotrope was prepared by Michler and Gradmann (*Ber.*, ·1877, *10*, 2079) by·the direct combination of dimethyl aniline and benzyl chloride. · *p*-Nitrobenzyl-phenyldimethyl ammonium chloride was· prepared in a similar way from *p*-nitrobenzyl chloride by Wedekind (*Annalen*, 1899, *307*, 287).

m-Nitrobenzyl chloride combines with dimethyl aniline more readily than the para compound (*cf.* Peacock, *J. Chem. Soc.*, 1925, *127*, 2179), and gives *m*-nitrobenzylphenyldimethyl ammonium chloride.

In ·the ·earlier experiments the phenol was dissolved in aqueous· caustic soda solution but it was later found ·that this was unnecessary and that benzylation proceeds quite smoothly, in the presence of sodium carbonate. The benzylation of the nitrophenols proceeds much·less

readily than does that of phenol. Salicylic acid was recovered unchanged from an attempt at benzylation.

Phenylbenzyl ether, was first prepared by Sintenin (*Annalen*, 1867, *143*, 81). The *ortho-* and *para*-nitrophenyl benzyl ethers and the *ortho-* and *para*-nitrobenzylphenyl ethers were prepared by Kump (*Annalen*, 1884, *224*, 104). by the action of the corresponding benzyl chloride upon the potassium salt of the corresponding phenol in alcoholic solution. Staedel (*Annalen*, 1883, *217*, 44) in a similar way prepared the benzyl ethers of the cresols and of α- and β-naphthols. Sintenin (*Annalen*, 1872, *161*, 345) obtained a chlorophenylbenzyl ether of m. p. 70-71°, by the chlorination of phenylbenzyl ether in the presence of mercuric oxide. He did not determine the constitution of this compound: I find that the melting point of *p*-chlorphenylbenzyl ether is 71°. Sintenin's compound therefore, is the *para* isomeride. The *o-*, *m-* and *p*-chlorphenylbenzyl ethers and the '2 : 4-dichlorphenylbenzyl ether seem to be new substances.

EXPERIMENTAL.

Phenylbenzyldimethyl ammonium chloride, *p*-nitrobenzylphenyldimethyl ammonium chloride and *m*-nitrobenzylphenyldimethyl ammonium chloride were prepared in the usual manner. *m*-Nitrobenzylphenyl dimethyl-ammonium chloride is new; m. p. 144°. (Found: Cl = 12·93. $C_{15}H_{17}N_2O_2Cl$ requires Cl = 12·13 per cent.)

The general method employed for benzylation can be illustrated by two examples.

α-*Naphthyl benzyl ether.*

α-Naphthol (7·3 g.) and benzylphenyldimethyl ammonium chloride (6·15 g.) in sodium carbonate solution (7 g. in 100 c.c.) were heated under a reflux condenser

for 4 hours. The mixture having been extracted with benzene, the extract was washed with caustic soda to remove naphthol and then with hydrochloric acid (1:1) to remove dimethylaniline. The extract was then dried over calcium chloride: after removal of the benzene the residue solidified to a mass of brownish crystals which when crystallized from alcohol formed colourless crystals, m. p. 74·5°-75°; Braun and Reich (*Annalen*, 1925, 445, 233) give the m. p. 61°. The yield of crude substance was 5 g. (Found : C=86·94; H=6·72. $C_{17}H_{14}O$ requires C=87·12; H=5·98 per cent.) The molecular weight determined by the depression of the freezing point was 240; calculated 234. Staedel (*loc. cit.*) obtained this compound as an oil.

Phenyl-p-nitrobenzyl ether.

Phenol (4·7 g.) and *p*-nitrobenzyl phenyldimethyl ammonium chloride (14·6 g.) were mixed with excess of caustic soda (15 c.c. of 4*N* caustic soda diluted to 50 c.c., and the mixture was heated under a reflux condenser for four hours. The mixture having been extracted with benzene was washed with caustic soda to remove unchanged phenol, then with hydrochloric acid (1:1) and finally with water. The benzene extract was then dried over calcium chloride. After removal of the benzene the residue, which was solid, was crystallized from alcohol; m. p. 91°. Kump (*loc. cit.*) gives m. p. 91°.

Phenylbenzyl ether prepared in a similar manner had the m. p. 39°. Sintenin (*loc. cit.*) gives m. p. 38°–39°.

Benzyl-*o*-cresyl ether, b. p. 284°; Staedel (*loc. cit.*) gives b. p. 285°-290°. Benzyl-*m*-cresyl ether, m. p. 43°; Staedel (*loc. cit.*) gives m. p. 43°. Benzyl-*p*-cresyl ether, m. p. 40° : Staedel (*loc. cit.*) gives m. p. 41°. Benzyl-*β*-naphthyl ether m. p. 99°-100°, Staedel (*loc. cit.*) gives

m. p. 99°. *Benzyl-o-chlorophenyl ether*, m. p. 296°. (Found : Cl=16·06; $C_{13}H_{11}OCl$ requires Cl = 16·24 per cent.) *Benzyl-m-chlorophenyl ether*, colourless crystals from alcohol, m. p. 59°. (Found: Cl = 16·6 per cent.) *Benzyl-p-chlorophenyl ether*, colourless crystals from alcohol ; m. p. 71°. (Found: Cl=16·59). *Benzyl-2 : 4-dichlorophenyl ether*, colourless crystals from alcohol ; m. p. 60°. (Found: Cl = 27·85. $C_{13}H_{10}OCl_2$ requires Cl = 27·78 per cent.) p-Nitrobenzylphenyl ether, m. p. 91°, Kump (*loc. cit.*) gives m. p. 91°. Benzyl-p-nitrophenyl ether, m. p. 106° (the yield was very small) ; Kump (*loc. cit.*) gives m. p. 106°.

Further experiments are in progress with other hydroxy substances, including celluloses, and with amines.

I wish to thank Professor D. H. Peacock for suggesting this work and for advice during its progress.

Condensation of o-Hydroxy Aromatic Alde-hydes with ω-Cyanacetophenone.

BY

SUBIMAL CHANDRA GHOSAL.

The work that is described in this paper was undertaken in the expectation of obtaining pyrilium derivatives containing the cyano group. For instance, salicylaldehyde, ω-cyanacetophenone and hydrochloric acid might react thus :—
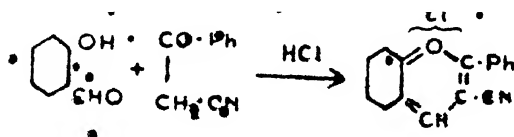
(compare Decker and Fellenburg, *Ber.*, 1907, *40*, 3815; Perkin, Robinson and Turner, *J. Chem. Soc.*, 1908, *93*, 1085; Robinson and collaborators, *J. Chem. Soc.*, 1922, *121*, 1577 and subsequent papers). In no case did the reaction give the expected product.

The reaction between an *o*-hydroxybenzaldehyde and ω-cyanacetophenone gives a benzoyl coumarin: when salicylaldehyde is used the product is identical with the 3-benzoylcoumarin prepared by Knoevenagel and Arndt (*Ber.*, 1904, *37*, 4497).

The formation of the coumarin derivatives is probably to be attributed to the interaction of the more reactive

cyano group with the phenolic hydroxy group according to the following scheme :—
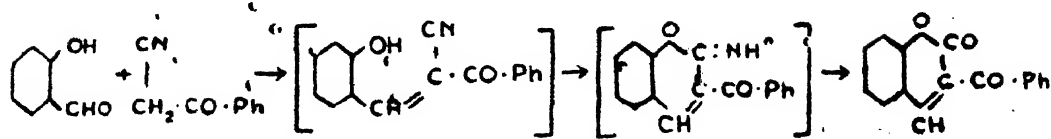
As it frequently happens in condensation of this type that an intermediate imino compound is formed (Lapworth, *J. Chem. Soc.*, 1925, *127*, 562), it appeared a matter of interest to examine whether by conducting the experiment in an anhydrous medium, so as to prevent the premature decomposition of the cyano group, the intermediate imino phase could be isolated. Experiments made in **this** direction, however, were unsuccessful.

EXPERIMENTAL.

3-*Benzoylcoumarin.*

Salicylaldehyde (3 g.) and ω-cyanacetophenone (4 g.) were dissolved in glacial acetic acid (30 c.c.). Dry hydrochloric acid was passed through the solution cooled to 0° for nearly four hours. The mixture was left over-night in a well-corked flask. Next morning the reddish brown contents were poured into a large excess of water and the solution was filtered from resinous matter. The filtrate on keeping deposited the condensation product in beautiful glistening needles. A further quantity was recovered from the resinous matter by treatment with dilute alcohol. The yield was 60 per cent. of the theoretical. When recrystallised from alcohol, it melted at 138° and was found to be identical with the 3-benzoyl-coumarin described by Knoevenagel and Arndt (*loc. cit.*): (Found : C = 76·6 ; H = 4·00. $C_{16}H_{10}O_3$ requires C = 76·8 ; H = 4·00 per cent.)

The *phenylhydrazone*, prepared in the usual manner, separated from alcohol as a yellow crystalline mass and melted at 95°-100° with decomposition. (Found: $N = 8 \cdot 27$. $C_{22}H_{16}O_2N_2$ requires $N = 8 \cdot 23$ per cent.)

6-*Nitro*-3-*benzoylcoumarin*.

3-Benzoylcoumarin (2 g.) was dissolved in concentrated sulphuric acid (20 c.c.). The solution was cooled to 0°, and treated with 60 c.c. of a mixture of 1 part of strong nitric acid and 3 parts of concentrated sulphuric acid. At the end of half an hour the product was poured on crushed ice and the precipitated mass collected.

It was purified by recrystallisation from glacial acetic acid. It melted at 200° and was identified by direct comparison with a specimen synthesised for the purpose (see below). (Found: $N = 4 \cdot 91$. $C_{16}H_9O_5N$ requires $N = 4 \cdot 74$ per cent.)

The position of the nitro group in the product described above was established by condensing ω-cyanaceto-phenone (4 gms.) with 5-nitro-salicylaldehyde (4·5 gms.) in the usual manner. The product separated from a mixture of alcohol and acetone in pale yellow needles melting at 200°.

8-*Methyl*-3-*benzoylcoumarin*.
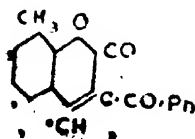
The reaction with o-homosalicylaldehyde was brought about exactly as in the case of salicylaldehyde. The product crystallised from dilute acetone in white feathery needles. It melted at 126°. (Found: $C = 77 \cdot 1$; $H = 4 \cdot 5$. $C_{17}H_{12}O_3$ requires $C = 77 \cdot 2$; $H = 4 \cdot 5$ per cent.) The

phenylhydrazone separated from alcohol as a yellow crystalline mass decomposing between 105° and 110°.

6-Methyl-3-benzoylcoumarin.
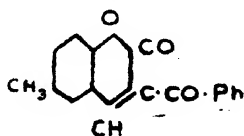
It was prepared in the usual way from *p*-homosalicyl-aldehyde (4 g.) and ω-cyanacetophenone (4 g.). The coumarin separated from alcohol in white needles and melted at 174°. (Found : C = 77·00 ; H = 4·5. $C_{17}H_{12}O_3$ requires C = 77·2 ; H = 4·5 per cent.)

7-Methyl-3-benzoylcoumarin.
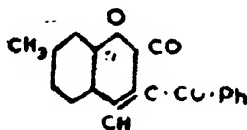
7-Methyl-3-benzoylcoumarin was prepared in the usual way from *m*-homosalicylaldehyde (4 g.) and ω-cyanacetophenone (4 g.). The coumarin separated from alcohol in white needles and melted at 142°. (Found : C = 77·01 ; H = 4·48. $C_{17}H_{12}O_3$ requires C = 77·2 ; H = 4·5 per cent.)

The *phenylhydrazone* separated from alcohol in yellow crystalline mass decomposing between 115° and 120°.

7-Hydroxy-3-benzoylcoumarin.
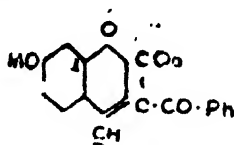
The yield of the condensation product using resor-cylaldehyde was unsatisfactory and only a small quantity

of it was obtainable after repeated treatment of the resinous product with dilute alcohol. It crystallised from alcohol in white needles; m. p. 241°. (Found: C = 71·96; H = 3·71. $C_{16}H_{10}O_4$ requires C = 72·18; H = 3·75 per cent.)

The *acetyl* derivative was prepared by boiling the coumarin with acetic anhydride and sodium acetate in the usual way. It separated from alcohol in needle-shaped crystals melting at 172°. (Found: C = 69·98; H = 3·82. $C_{18}H_{12}O_5$ requires C = 70·12; H = 3·89 per cent.)

3-Benzoyl-β-naphthapyrone.
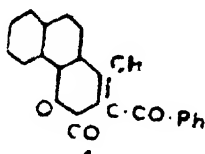
The condensation with 1:2-naphtholaldehyde took place readily. The product, light yellow needles, on recrystallisation from glacial acetic acid melted at 215° and evidently consisted of the 3-benzoyl-β-naphthapyrone described by Kurt Bartsh (*Ber.*, 1903, *36*, 1974). (Found: C = 79·7; H = 3·99. $C_{20}H_{12}O_3$ requires C = 80·00; H = 4·0 per cent.)

My best thanks are due to Principal H. E. Stapleton and Prof. R. N. Sen for their kind interest in the work.

Complex Iodates of Tin and Antimony.

BY

PRIYADARANJAN RÂY AND SOURINDRA NATH RAY.

No iodates of tin and antimony have yet been described. The present investigation was therefore undertaken with a view to prepare the iodates of these metals and study their properties.

By the action of a nitric acid solution of iodic acid on penta-hydrated stannic chloride stanni-iodic acid (I) or di-hydroxy-tetra-iodato stannic acid (II) was obtained according to the proportions of iodic acid used. When stanni-chlorides of the alkali metals were substituted for the hydrated stannic chloride, compounds of the type (IV, salts corresponding to I) were invariably obtained. With sodium iodate stannic chloride gave tetra-hydroxy-di-iodato stannic acid (III) ; while potassium iodate and potassium stannichloride gave a double compound (V) of hexa-iodato potassium stannate with mono-hydroxy-penta-iodato potassium stannate.

$$[Sn(IO_3)_6]\cdot H_2 ; \qquad [(HO)_2Sn(IO_3)_4]H_2$$
$$\text{I} \qquad\qquad \text{II}$$

$$[(HO)_4Sn(IO_3)_2]H_2 ; \qquad [Sn(IO_3)_6]M_2 ,$$
$$\text{III} \qquad\qquad \text{IV}$$

$$(M = Li, Na, K, Rb, Cs \text{ or } NH_4)$$

$$K_2[Sn(IO_3)_6].K_2[(HO)Sn(IO_3)_5]$$
$$\text{V}$$
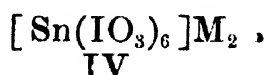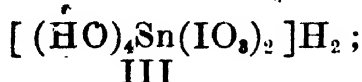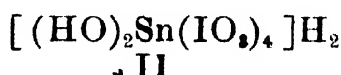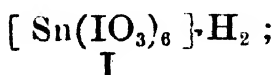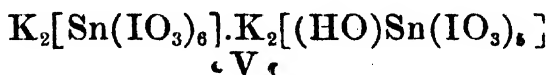
By the calcination of (I) a substance was obtained corresponding to the empirical formula, $Sn_{14}O_{21}I$. This

substance is characterised by its extreme stability and its insolubility in any solvent.

Iodic acid and chloro-antimonic acid give a compound of the composition $[(HO)_3Sb(IO_3)_3]H$, trihydroxy tri-iodato antimonic acid.

Considering the analogy between H_2SnCl_6 and H_2PtCl_6 and between their products of hydrolysis, and recalling the resemblance of stannic acid and stannates with $H_2Pt(OH)_6$ and its salts, the constitution of these iodates may be represented according to the above scheme (cf. Werner and Pfeiffer, Zeit. anorg. Chem., 1898, 17, 182; Pfeiffer, Ber., 1905, 38, 2466; Belluti and Parravano, Atti. R. Accad. Lincei, 1904, (v), 13 (ii), 307, 324; ibid, 1905, (v), 14 (i), 457; Zeit. anorg. Chem., 1905, 45, 142).

Experimental.

Di-hydroxy-tetra-iodato Stannic Acid (II).

The compound was obtained in a granular form by adding to a slight excess of iodic acid dissolved in dilute nitric acid (concentrated acid of sp. gr. 1·4 diluted with an equal volume of water) a calculated amount of a solution of pentahydrated stannic chloride crystals in water acidified with a drop of strong hydrochloric acid and evaporating the clear liquid on the water-bath. The mixture was then cooled and the substance was washed three times by decantation with dilute nitric acid (10 c.c. concentrated acid per 100 c.c. water), filtered and washed several times on the funnel with the same liquid. The substance was then dried in vacuum over sulphuric acid.

Found (sample dried overnight): Sn = 13·54; HIO_3 = 79·00.

Found (Sample dried for several days): $Sn = 14.12$; $HIO_3 = 81.45$. $Sn(IO_3)_4$. $2H_2O$ or $H_4[Sn(OH)_2(IO_3)_4]$ requires $Sn = 13.92$; $HIO_3 = 81.87$ per cent.

Stanni-iodic Acid (I).

To a large excess of iodic acid dissolved in dilute nitric acid (20 c.c. concentrated acid per 100 c.c.), the calculated amount of stannic chloride solution (*cf.* previous preparation) was added drop by drop with constant stirring; the mixed solution was then evaporated on the water-bath when a crystalline white powder was obtained. The mixture was then cooled and the crystals washed and filtered as in the previous case. They were then dried in vacuum over sulphuric acid. (Found: $Sn = 10.24$, 10.25; $IO_3' = 88.84$, 89.04. $Sn(IO_3)_4$. $2HIO_3$ requires $Sn = 10.16$ and $IO_3' = 89.6$ per cent.).

Potassium Stanni-iodate.

Potassium stannichloride dissolved in the least quantity of water was added to a solution of iodic acid in dilute nitric acid (10 c.c. concentrated acid per 100 c. c.), with constant stirring. A granular precipitate was readily obtained which was washed with dilute nitric acid of the same strength and dried in vacuo over sulphuric acid. (Found: $Sn = 9.58$, 9.38, 9.61; $IO_3' = 83.73$, 83.8; $K = 6.16$, 6.32. $Sn(IO_3)_4$. $2KIO_3$ requires $Sn = 9.54$; $IO_3' = 84.2$ and $K = 6.62$ per cent.)

Ammonium Stanni-iodate.

The curdy white precipitate obtained by mixing the calculated amount of ammonium stannichloride with an excess of iodic acid was dissolved by adding concentrated nitric acid. Concentrated ammonia was then added to partially neutralise the excess of free nitric acid. A

granular precipitate formed and readily settled. It was then washed and dried as in the previous case. (Found: $Sn = 9.93$, 10.0; $IO_3' = 86.8$, 86.98; $NH_4 = 3.05$. $Sn(IO_3)_4$. $2 NH_4IO_3$ requires $Sn = 9.87$; $IO_3' = 87.14$ and $NH_4 = 2.99$ per cent.)

Rubidium Stanni-iodate.

Rubidium stannichloride dissolved in a fairly dilute nitric acid was added to a solution of an excess of iodic acid in the same solvent. The stanni-iodate separated in a fine granular form on standing for some time. The substance was then washed and dried as in the case of the potassium compound. (Found: $Rb = 12.85$; $Sn = 8.76$; $IO_3' = 77.7$. $Sn(IO_3)_4$. $2RbIO_3$ requires $Rb = 12.76$; $Sn = 8.88$ and $IO_3' = 78.33$ per cent.)

Cæsium Stanni-iodate.

Cæsium stannichloride dissolved in moderately strong nitric acid was slowly added to an excess of dilute nitric acid solution of iodic acid. The mixed solution was evaporated on the water-bath when granular white precipitate gradually separated out. The precipitate was washed and dried as in the previous case. (Found: $Cs = 18.11$; $Sn = 8.33$; $IO_3' = 72.85$. $Sn(IO_3)$. $2Cs(IO_3)$ requires $Cs = 18.53$; $Sn = 8.35$ and $IO_3'' = 73.17$ per cent.)

Sodium Stanni-iodate.

A solution of sodium stannichloride, acidified with a drop of dilute nitric acid, was gradually added to a solution of an excess of iodic acid in moderately strong nitric acid (concentrated acid diluted with an equal volume of water) with constant stirring. The solution on concentration on the water-bath gave a granular precipitate which was filtered on the pump, washed several times with dilute nitric acid (6 c.c. of concentrated acid, sp. gr. 1.4 per 100 c.c.) and dried as usual. (Found:

Na$=3.95$; Sn$=10.04$; IO$_3=86.18$., Sn(IO$_3$)$_4$ ·2NaIO$_3$ requires Na$=3.78$; Sn$=9.8$ and IO$_3'=86.1$ per cent.)

Lithium Stanni-iodate.

About 8 gms. of iodic acid were dissolved in fairly strong nitric acid. (35 c.c. of concentrated acid per 100 c.c.). Two gms. of stannic chloride and 6 gms. of lithium chloride dissolved in about 10 c.c. of water were added drop by drop to the solution of iodic acid. The mixed solution, on evaporation on the water-bath, gave a crystalline precipitate. It was filtered, washed and dried as in the case of the sodium compound. (Found : Li $= 1.13$; Sn $= 10.12$; IO$_3'=87.88$; Sn(IO$_3$)·2LiIO$_3$ requires Li$=1.18$; Sn$=10.06$; IO$_3'=88.76$ per cent.)

Double Compound of Hexa-iodato Potassium Stannate and Mono-hydroxy-penta-iodato Potassium Stannate (V).

When potassium iodate was substituted for iodic acid in the preparation of potassium stanni-iodate, a compound was obtained which on analysis gave the following results and differed from potassium stanni-iodate in composition. (Found : K $= 6.75$, 6.8 ; Sn $=10.28$, 10.24 ; IO$_3'=81.58$, 81.45. K$_2$Sn(IO$_3$)$_6$·K$_2$Sn(IO$_3$)$_5$(OH) requires K· $= 6.68$; Sn $= 10.19$ and IO$_3'=82.44$ per cent.)

Tetrahydroxy-di-iodato Stannic Acid (III).

To an excess of sodium iodate dissolved in dilute nitric acid (10 c.c. of strong acid per 100 c.c.) was added a solution of the calculated amount of stannic chloride in the least amount of water. A thick white precipitate was obtained which was allowed to settle, filtered, washed with dilute nitric acid and dried as usual. (Found : Sn$=22.11$, 21.9 ; IO$_3'=66.5$, 66.6 ; I $= 46.96$. Sn(IO$_3$)$_2$ (OH)$_2$·2H$_2$O requires Sn$=22.07$; IO$_3'=65.33$ and I$=47.17$ per cent.)

Properties of Stanni-iodic Acids and their Salts.

With the exception of hexa-iodato acid and its lithium salt, the compounds are all amorphous, white powders. They all react acid to litmus. Like most of the iodates they are insoluble in water but are gradually hydrolysed by it being completely broken by boiling water into stannic oxide and iodic acid or alkali iodates. They are easily reduced by reducing vapours and organic matters, with liberation of iodine. The freshly prepared lithium and sodium stanni-iodates are soluble in dilute and strong nitric acids but on drying they completely lose this property.

Action of Heat on Hexa-iodato Stannic Acid.

When the hexa-iodato stannic acid was ignited in a porcelain crucible, copious vapours of iodine were given off and a light yellow residue was left even after strong ignition over the full flame of a Teclu burner. There was no loss of tin during the ignition as the *total* amount of it remained unchanged in the ignited product. The residue was unaffected by water, alcohol, sulphur dioxide, chloroform, carbon tetrachloride and carbon bisulphide. Different samples of the ignited residue on analysis gave a fairly constant composition. (Found :. $Sn = 77.57$, 77.89; $I = 5.95$, 5.99. $Sn_{14}O_{21}I$ requires $Sn = 78.25$ and $I = 5.96$ per cent.)

Trihydroxy-tri-iodato Antimonic Acid.

A solution of antimony pentachloride in strong hydrochloric acid was slowly added to an excess of a concentrated aqueous solution of iodic acid. A precipitate appeared after stirring for a few seconds. It was filtered on the pump and washed with a small amount of water. It was then dissolved in excess of water acidulated with

a few drops of dilute iodic acid and evaporated on the water-bath when a white powder separated from the solution. It was filtered, and washed as before and dried over sulphuric acid in vacuum. (Found: $Sb=17\cdot13$, $17\cdot1$; $IO_3'=74\cdot41$, $73\cdot86$; $I=53\cdot71$. $Sb(IO_3)_3(OH)_2\cdot H_2O$ requires $Sb=17\cdot21$, $IO'_3=75\cdot31$ and $I=54\cdot66$ per cent.)

The substance is an amorphous white powder and reacts acid towards litmus. It is soluble in water and the solution remains clear even after addition of ammonia; while cold dilute caustic soda solution slowly precipitates the oxide of antimony, concentrated nitric acid also precipitates hydrated antimonic oxide from the solution.

METHOD OF ANALYSIS.

Stanni-iodates.

The substance was treated with hydrochloric acid mixed with a little sulphurous acid to reduce the iodate. The solution was then carefully neutralized with ammonia and then the tin was precipitated as SnO_2 by boiling with ammonium nitrate. The alkali metals were estimated as sulphate by evaporating the filtrate with a little sulphuric acid. Iodic acid was estimated by treating the substance with a solution of potassium iodide in hydrochloric acid and titrating the liberated iodine with sodium thiosulphate. Iodine was also estimated as silver iodide in the filtrate from tin oxide by first decomposing the substance with sulphurous acid alone.

The substance $Sn_{14}O_{21}I$ was analysed by fusing with sodium carbonate and sulphur. Tin was precipitated as sulphide from the solution of the fused mass in water by the addition of acetic acid. Iodine was estimated as silver iodide from the filtrate after removing the sulphuretted hydrogen by evaporation and finally by oxidation with a little ammonical hydrogen peroxide.

Antimony Compounds.

The substance was dissolved as in the case of tin iodate by a mixture of hydrochloric and sulphurous acid. The solution was treated with an excess of yellow ammonium sulphide and the antimony was precipitated as sulphide by adding acetic acid. By decomposing the substance with sulphurous acid alone iodine was also estimated as silver iodide from the filtrate from antimony sulphide. Iodic acid as such was determined by treating the substance with an acid solution of potassium iodide as in the case of tin compounds but in this case as both antimonic (Sb^v) antimony and iodic acid contributed to the liberation of iodine so the amount corresponding to the reduction of antimony from the pentavalent to the trivalent condition was deducted from the total amount of iodine liberated.

Metallic Compounds of Rubeanic Acid.

By

Priyadaranjan Ray and Ramani Mohan Ray.

Rubeanic acid may be regarded as a tautomeric compound consisting of an equilibrium mixture of sym.-dithio-oxamide and sym.-di-imido-dithio-oxalic acid. (Wallach and Reinhardt, *Annalen*, 262, 354; Ephraim, *Ber.*, 1891, 24, 1026). Sodium and lead salts of the acid are mentioned in the literature (*Ber.*, 1880, 13, 528; *Annalen*, 38,315). In this paper a systematic investigation of other metallic derivatives has been undertaken.

Rubeanic acid readily gives insoluble precipitates with salts of silver, gold, platinum, zinc, cobalt and nickel. The copper, cobalt and nickel compounds have been prepared and studied, and found to have the formula $MeC_2H_2N_2S_2$ (Me=metal). Unlike the lead and sodium salts, the metallic atom in these compounds seems to form the centre of a cyclic co-ordination complex, as indicated in the structural formula given below.
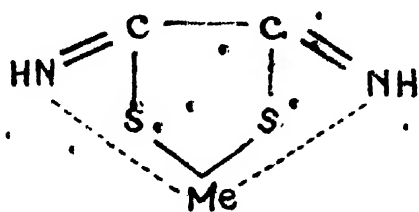
(Me=Cu, Co++ or Ni).

The reasons for such an assumption are :—

(*i*)   These compounds are fairly stable and can be heated up to 160° without decomposition, whereas the compounds with sodium, lead (*loc. cit.*) and silver—metals which possess very little residual affinity—are extremely unstable.

(*ii*) These salts possess characteristic colours differing from those of the usual organic and inorganic salts of cobalt and nickel: copper rubeanate being black, the nickel salt bluish-violet and the cobalt compound reddish-brown.

(*iii*) The nickel and cobalt salts on digestion with caustic soda solution partially dissolve and the rubeanates are reprecipitated from these solutions on neutralisation of the alkali.   The solutions are unaffected by sulphuretted hydrogen or ammonium sulphide.

(*iv*) With a strongly ammoniacal solution of nickel salts, rubeanic acid gives a brilliant red compound, which readily gives up ammonia and changes to the bluish-violet nickel rubeanate.   Also, the latter dissolves in liquor ammonia to a deep orange-red solution from which the original rubeanate is obtained on boiling off the ammonia.   The orange-red solution does not, however, contain free nickel or rubeanic acid radical and is, no doubt, due to a combination of nickel rubeanate with further molecules of ammonia.   Recalling that nickel tetrammino compounds are stabler than hexammino derivatives, the formula given above, which shows the co-ordination number of nickel to be four, explains the fugitive nature of the red compound in which the nickel atom has possibly a co-ordination number of six.

As might be expected from the structure assigned to these compounds, they are extremely insoluble in water and in all the ordinary organic solvents, 1 part of

nickel in 500,000, 1 part of copper in 1,000,000 and 1 part of cobalt in 150,000 parts of water being immediately precipitated as rubeanates. In fact, nickel and cobalt have been successfully estimated by precipitation as rubeanates; while copper presented some difficulties as regards washing and filtering. With more dilute solutions of copper, nickel and cobalt, rubeanic acid produces characteristic green, blue and yellow colourations respectively; and the sensitiveness of these reactions as tests for the micro-detection of these metals has been determined. The colour-effects can be used to detect 1 part of copper in 30 million, 1 part of nickel in 7 million and 1 part of cobalt in 30 million parts of water.

Carbonato-tetrammino-cobaltic nitrate with rubeanic acid gives tetra-aquo-diammino-tri-rubeanato-dicobalt $[Co_2(H_2O)_4(NH_3)_2(Rb)_3]$, where $Rb = (C_2H_2S_2N_2)''$. It loses the water molecules when heated to 115-120° and is converted into

$$[(Rb)\equiv Co - Rb - Co \equiv (Rb)].$$
$$NH_3 \qquad NH_3$$
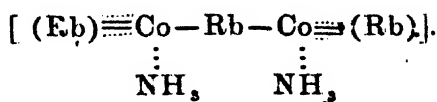
EXPERIMENTAL.

The rubeanic acid used in these experiments was prepared by passing a rapid current of dry and pure cyanogen gas (free from carbon dioxide) into a freshly-prepared, ice-cold solution of potassium hydrosulphide in absolute alcohol and acidifying the saturated solution with dilute hydrochloric acid (*cf.* Ephraim, *Ber.*, 1889, 22, 2305). The yield was about 76% of the theoretical. (Found : N=23·26. Calc., N=23·33 per cent.).

Copper Rubeanate.

The compound was precipitated by adding an alcoholic solution of rubeanic acid to a slight excess of copper sulphate solution, washed by decantation with warm water, filtered on the pump and dehydrated at 105°. Samples prepared, in aqueous or ammoniacal solutions, as also in presence of sodium acetate, gave the same composition. (Found: $Cu = 33\cdot3$, $33\cdot2$; $S = 32\cdot85$, $32\cdot6$; $N = 14\cdot83$, $15\cdot15$. $CuC_2N_2S_2H_2$ requires $Cu = 35\cdot0$; $S = 35\cdot2$; $N = 15\cdot4$ per cent.).

The results of analysis were always lower than the theoretical values due to adsorption of electrolytes which could not be removed even by prolonged washing.

Properties.—Copper rubeanate when freshly precipitated, was a voluminous, slimy, black mass which changed to black, shining scales on drying. It was fairly stable and began to decompose above 160°. When heated, a red liquid distilled over and condensed in the cooler parts of the tube. On heating more strongly the red liquid also decomposed with evolution of sulphur dioxide, ammonia and cyanogen; while a residue of copper oxide was left behind. It was unaffected by ammonia but dissolved in moderately dilute, boiling hydrochloric acid. Boiling caustic alkalis decomposed it into copper sulphide, alkali cyanide and sulphocyanide.

Nickel Rubeanate.

To an aqueous solution of a nickel salt was added the requisite amount of an alcoholic solution of rubeanic acid. There was no precipitation at this stage, but on neutralising the acid liberated during the reaction with the minimum amount of ammonia or sodium acetate, the rubeanate

at once separated out. This was washed by decantation, filtered on the pump and dried at 100°. With a strongly ammoniacal solution of nickel salt, rubeanic acid formed an intensely red compound; but the latter readily changed into the bluish-violet rubeanate even when filtered and desiccated in an atmosphere of ammonia. The bluish-violet rubeanate gave the following results on analysis. (Found: $Ni = 33 \cdot 1$; $S = 36 \cdot 6$; $N = 16 \cdot 3$. $NiC_2H_2N_2S_2$ requires $Ni = 33 \cdot 2$; $S = 36 \cdot 2$; $N = 15 \cdot 8$ per cent.)

Properties.—Nickel rubeanate was precipitated as a slimy mass which changed to a bluish-violet powder on drying. It was fairly stable and decomposed above 160°. It behaved like copper rubeanate on dry distillation.

It was insoluble in water and the common organic solvents; but in pyridine it dissolved to a pink solution, the colour being discharged by water. It was also soluble in dilute hydrochloric acid, specially on boiling.

It dissolved partially in 8% ammonia to a bluish-violet solution and more freely in strong ammonia to a deep orange-red solution which contained no $-CNS'$, $-S''$ or C_2O_4'' ions, nor did it give any tests for free nickel or free rubeanic acid. From this solution the original bluish-violet rubeanate was reprecipitated on boiling off the ammonia.

It dissolved in caustic alkali to a yellowish-red solution changing to pink on dilution. From these solutions the bluish-violet nickel rubeanate was obtained by neutralisation, on standing overnight or by prolonged boiling. The solutions were unaffected by H_2S or $(NH_4)_2S$ and did not contain any $-CNS'$, $-CN'$, Ni^{++}, C_2O_4'' or $C_2N_2S_2H_2''$ ions. These facts proved that caustic alkali did not decompose the rubeanate molecule and that the solvent action was therefore due to some sort of salt-formation like $NiC_2S_2N_2Na_2$

Estimation of Nickel.

The nickel was precipitated as rubeanate, in the presence of sodium acetate or ammonia, the precipitate was washed by decantation with hot water, filtered, dried and ignited. The rubeanate decomposed into NiS which changed on further ignition to NiO (cf. Cormimboef, *Annali. Chim. Appl.*, 1906, 2, 6). Part of the oxide was reduced to the metallic state by the organic matter. The ignited mass was therefore treated with concentrated nitric acid, the excess of acid evaporated off, the nitrate was heated with a low flame, the temperature being gradually raised to a dull red heat, whereupon the conversion into nickel oxide was complete—the nickel being weighed as NiO. The results obtained are tabulated below.

Ni taken (gms.).	NiO found (gms.).	Ni found (gms.).	Error (gms.).
0·0201	0·0258	0·0203	+ 0·0002
0·0281	0·0362	0·0285	+ 0·0004
0·0321	0·0413	0·0325	+ 0·0004
0·0321	0·0408	0·0321	0·0000
0·0348	0·0441	0·0347	− 0·0001
0·0361	0·0460	0·0362	+ 0·0001
0·0503	0·0635	0·0499	− 0·0004
0·0571	0·0732	0·0575	+ 0·0004
0·0428	0·0545	0·0429	+ 0·0001
0·0371	0·0475	0·0374	+ 0·0003
0·0371	0·0476	0·0374	+ 0·0003
0·0497	0·0634	0·0409	+ 0·0002
0·0618	0·0791	0·0622	+ 0·0004
0·0412	0·0528	0·0415	+ 0·0003

Cobalt Rubeanate.

This compound was prepared, washed and filtered as in the case of nickel. Cobalt rubeanate settled more readily and was easily washed free from soluble matters. It could not be dehydrated even at 120°. (Found : Co=27·2 ; S=30·0 ; N=13·2. $C_2H_2N_2S_2Co, 2H_2O$ requires Co=27·7 ; S=30·1 and N=13·1 per cent.).

Properties.—Cobalt rubeanate was obtained as a reddish-brown, hygroscopic powder that did not lose all its water even at 130°. It began to decompose above 160° and behaved like the copper salt on strong heating, a mixture of cobalt sulphide and cobalt oxide being left behind as a residue. Like the nickel salt, it dissolved undecomposed in hot dilute alkali. It was unaffected by ammonia.

Estimation of Cobalt.

The cobalt was precipitated as rubeanate in the presence of sodium acetate or dilute ammonia ; the precipitate was washed with hot water, filtered, dried and ignited. The ignited mass was then treated with a few drops of concentrated nitric and one drop of concentrated sulphuric acids, converted into and weighed as $CoSO_4$ with the usual precautions. The results obtained are tabulated below.

Co taken (gms.).	CoSO₄ found (gms.).	Co found (gms.).	Error (gms.).
0·0208	0·0552	0·0210	+ 0·0002
0·0208	0·0548	0·0209	+ 0·0001
0·0208	0·0542	0·0206	−0·0002
0·0208	0·0550	0·0209	+ 0·0001
0·0416	0·1090	0·0415	−0·0001
0·0416	0·1094	0·0416	0·0000
0·0241	0·0636	0·0242	+ 0·0001
0·0271	0·0710	0·0270	−0·0001
0·0146	0·0385	0·0147	+ 0·0001
0·0312	0·0825	0·0314	+ 0·0002

Presence of ammonium salts and of metals of the fourth (analytical) group did not interfere with the estimation of cobalt and nickel by these methods.

The behaviour of rabeanic acid towards other metals is given below.

Silver nitrate gave a yellow ppt. which passed at once into black silver sulphide.

Mercurous salts gave a white ppt. even from strongly acid solutions. The precipitation was quantitative.

Mercuric salts behaved similarly. The precipitate consisted of an indefinite mixture of rubeanic acid and HgCl'.

Cadmium salts gave a yellowish-white ppt. only in presence of sodium acetate. It was soluble in acids and was decomposed by alkalis into CdS, NaCN and NaSCN. The compound changed slowly in the cold and more rapidly on boiling into CdS.

With zinc a white ppt. was obtained in neutral solution only. It behaved like the cadmium compound towards acids and alkali.

Gold and platinum gave brownish-black precipitates.

Tetra-aquo-di-ammino-tri-rubeanato-dicobalt.

To a solution of 4 g. of carbonato-tetrammino-cobaltic nitrate in 120 c.c. of water made ammoniacal with 40 c.c. of 8% ammonia was added an alcoholic solution of 1 g. of rubeanic acid (about a third of the theoretical amount) with constant stirring. There was an instantaneous precipitation. The precipitate was allowed to settle, washed with very dilute ammonia, filtered on the pump and dried in vacuo over sulphuric acid. (Found: Co = 20·64, 20·46; S' = 32·8, 33·1; N = 19·5, 18·95; Loss on drying

at 115-20° = 11·9. Co $(C_2N_2S_2H_2)_3$ $(H_2O)_4$ $(NH_3)_3$ requires Co = 20·4 ; S = 33·2 ; N = 19·3 ; H_2O = 12·3 per cent.).

The compound was obtained as a dull brown powder insoluble in water, dilute hydrochloric acid and the usual organic solvents. Boiling alkalis decomposed it with evolution of ammonia. The compound did not contain nitrate or carbonate radicles, and the cobalt was in the cobaltic condition. The substance after being dried at 115-20° gave, on analysis, N = 21·2. $Co(C_2N_2S_2H_2)_3$ $(NH_3)_2$ requires N = 21·7 per cent.

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The Decomposition of Potassium Mangani-oxalate in Plane Polarised, Circularly Polarised and Ordinary Light.

BY

JNANENDRA CHANDRA GHOSH AND A. N. KAPPANNA.

Christiansen (*Zeit. anorg. Chem.*, 1911, *27*, 325) describes a method for the preparation of crystals of pure manganic acetate and observes that when manganic acetate is dissolved in a concentrated solution of potassium oxalate a solution of deep red colour is obtained due to the formation of potassium mangani-oxalate. He was also able to obtain crystals of this salt, but they decomposed in the dark and very rapidly in light.

Werner found that potassium cobalti-oxalate, as generally prepared, is a racemic mixture and he succeeded in resolving it into its optically active varieties. Potassium mangani-oxalate must also, according to Werner's theory, be a racemic mixture of asymmetric molecules. In some previous investigations in this laboratory the influence of the state of polarisation of light on the velocity of photochemical reactions resulting in the formation of asymmetric molecules has been studied. (Ghosh and Purkayastha, *J. Indian Chem. Soc.*, 1925, 2, 261). In this reaction, however, it is the asymmetric molecules which undergo decomposition under the influence of light into inactive components. It has been observed that the velocity of decomposition for the same intensity of plane polarised and ordinary light is almost the same; circularly polarised light appears to be a little more effective, but this statement cannot be made with

confidence as the temperature of the reaction chamber could only be kept constant within $\pm 0.2°C$ when working at $6°C$. This reaction is an ideal one for the application of Einstein's law of photochemical equivalence, in that a molecule by absorption of light disintegrates of itself without any side reaction and it has been found that under favourable conditions, one quantum actually transforms one molecule.

EXPERIMENTAL.

The room temperature at Dacca varies from $25°$ to $33°$ and at these temperatures the velocity of decomposition of potassium mangani-oxalate in the dark was found to be very large; in fact it very largely masks the effect of light on the velocity of this decomposition. The decomposition in the dark was found to have a large temperature coefficient and it was felt that if photochemical reaction could be carried out at low temperatures the effect of the dark reaction would be comparatively small. The problem is to allow a parallel beam of light to enter a glass reaction vessel, maintained at a low temperature, without undergoing distortion or considerable loss in intensity. It is therefore necessary to avoid completely the deposition of dew on the glass windows of the low temperature enclosure in which the reaction vessel is kept. This is a difficult affair in a moist tropical country. After various unsuccessful devices were attempted, the following experimental arrangement gave satisfactory results.

A small water-tight brass box covered with ebonite sheets on the exterior, with glass windows on four sides and with a close fitting sliding top made also of ebonite contained the stoppered reaction vessel (1.65 cm. cube). Cold clear water from a thermostat maintained at the

To Thermostat

Pencil of light

cell

Cold water

ebonite

Water at room temperature

From Thermostat
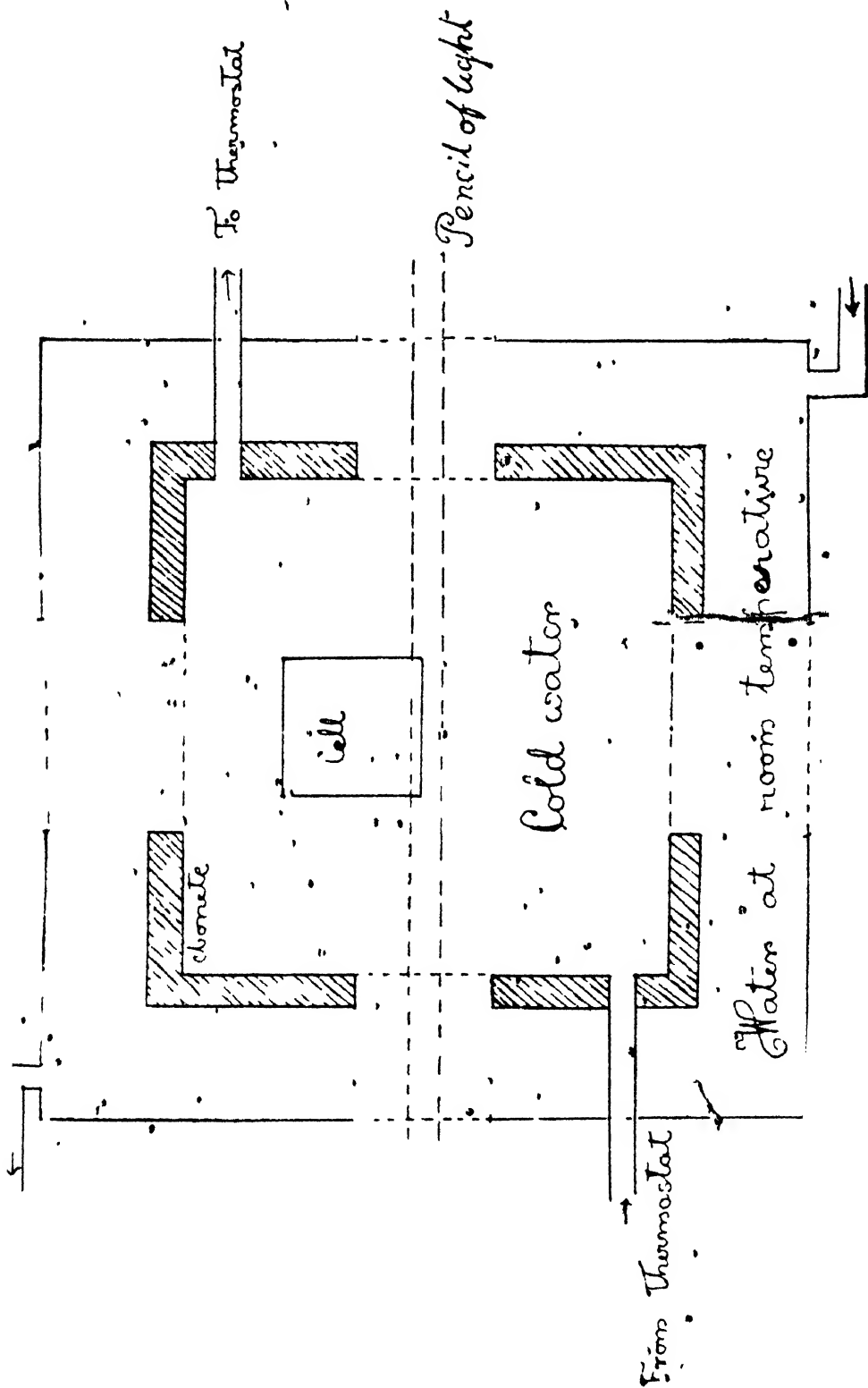
FIG. 1

desired low temperature was made to flow through this box by means of a circulating pump run by a hot air motor. This ebonite covered box was then placed inside a larger box of copper fitted with glass windows on four sides, through which distilled water at room temperature was circulated very rapidly (Fig. 1). The cold glass windows of the inner ebonite covered box are thus always in contact on the outside with distilled water at room temperature, and the light in entering these windows does not suffer any scatterring. The larger copper box is so fixed on the stage of a König-Marten spectrophotometer that one of the two parallel pencils into which the light from the source is split up, passes through the reaction vessel placed inside the ebonite covered box and the other pencil passes only through the cold water circulating in the box. The experimental arrangement is in other respects analogous to that used in the investigation of the photobromination of stilbene and of cinnamic acid in this laboratory (Ghosh and Purkayastha, loc. cit.). Only in this instance a 500 c. p. pointolite lamp was used. A thermometer passing through a hole on the ebonite box indicated the temperature of the reaction vessel. Its temperature was kept constant within $\pm 0.2°$ during the experiment while working at $6°C$ and within $\pm 0.1°$ at higher temperatures.

A solution of potassium mangani-oxalate at the desired temperature was obtained by dissolving a weighed quantity of manganic acetate in a given volume of potassium oxalate solution of known strength previously cooled to the temperature of the cold water in the thermostat. The reaction vessel was quickly filled with the cold solution of potassium mangani-oxalate, stoppered and placed inside the box. The circulating pump was started and the screen cutting off the light from the pointolite lamp removed.

Molecular Extinction Coefficients of Potassium Mangani-Oxalate in various Regions of the Spectrum.

Potassium mangani-oxalate in solution is coloured pinkish red and has been found to have absorption in all the regions of the spectrum. The extinction coefficients were measured by the rotation of the angle in the König-Marten spectrophotometer and calculated from the equation,

$$\epsilon = \frac{\log_{10}\tan a_1 - \log_{10}\tan a}{ct},$$

The values were obtained by examining an $M/800$ solution. The absorption being very great in all regions excepting red, orange and yellow, more concentrated solutions could not be employed. The results are given in Table 1 and are plotted in Fig. 2.

TABLE I.

Wave-length.	ϵ	$\log \epsilon$
6563	32·25	1·5086
6110	43·10	1·3345
5790	90·00	1·9542
5461	178·0	2·2504
5015	254·0	2·4048
4861	266·7	2·4260
4471	151·7	2·1810

Table II gives the values for $\log_{10}\tan a_1 - \log_{10}\tan a_2$ for various concentrations of potassium mangani-oxalate at wave-length $579\mu\mu$. In this region of the spectrum Beer's law is obeyed as will be at once obvious from Fig. 3 where the curve giving the values of $\log_{10}\tan a_1 - \log_{10}\tan a_2$, plotted against concentration, is found to be a
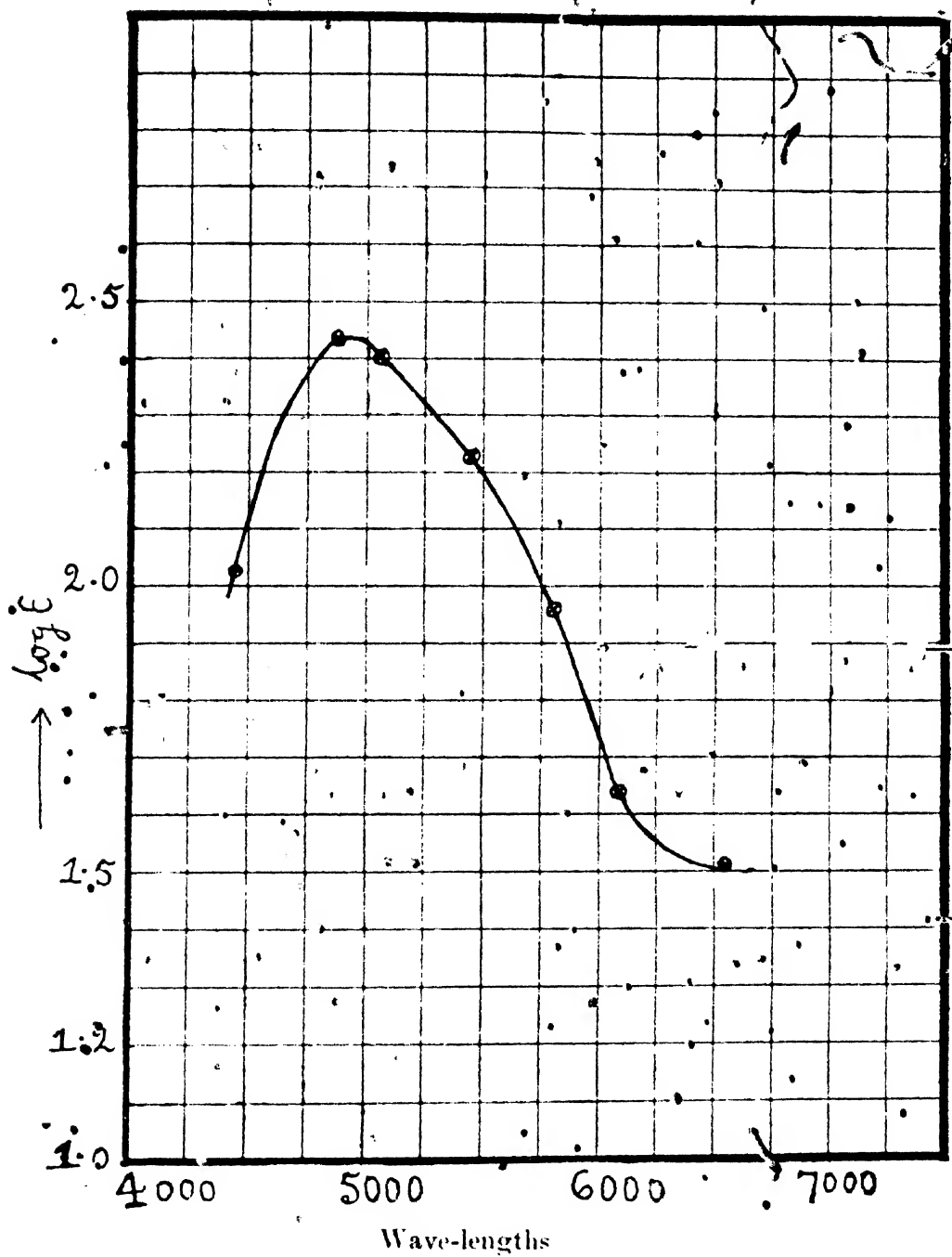
FIG. 2.
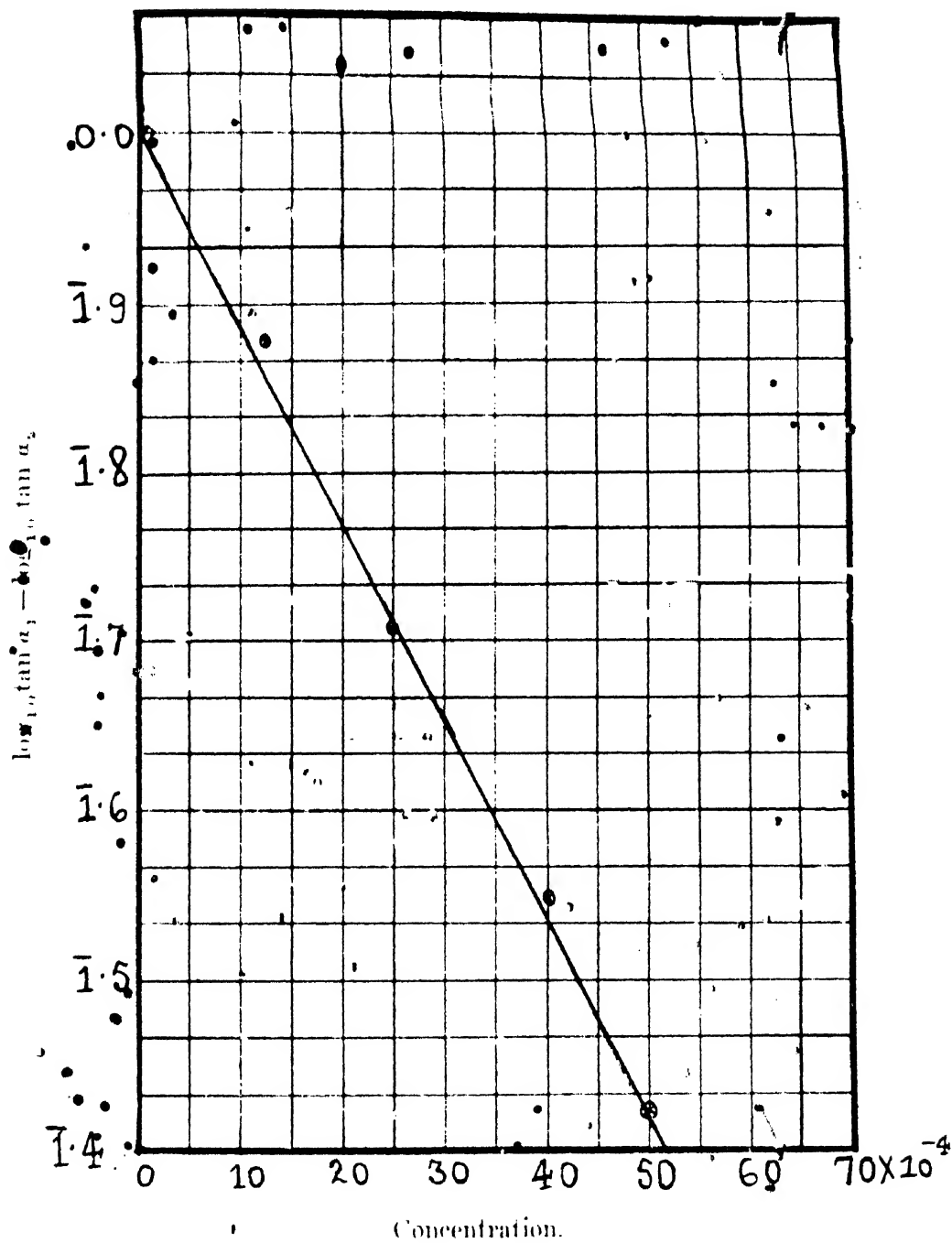
Fɪɢ 3

straight line. Readings to test Beer's law in regions of shorter wave-length could not be taken owing to very great absorption. It is clear that from the readings in the spectrophotometer for the above wave-length the concentrations can conversely be calculated.

TABLE II.

Concentration.	$\log_{10}\tan a_1 - \log_{10}\tan a_2$.
$50 \times 10^{-4} M$	$\bar{1}\cdot4254$
$40 \times 10^{-4} M$	$\bar{1}\cdot5493$
$25 \times 10^{-4} M$	$\bar{1}\cdot7035$
$12\cdot5 \times 10^{-4} M$	$\bar{1}\cdot8657$

Velocity Measurements at 6°C.

Even at 6°, the temperature at which the experiments were carried out, potassium mangani-oxalate decomposes pretty rapidly in the dark and the rate of this reaction was first measured. Table III gives the results of this measurement, k being the velocity constant of mono-molecular reaction.

TABLE III.

Time in minutes.	Conc. $\times 10^5$	k
0	$43\cdot25$	...
30	$37\cdot25$	$0\cdot004968$
60	$32\cdot00$	$0\cdot005014$
90	$27\cdot25$	$0\cdot005129$
120	$23\cdot25$	$0\cdot005152$
		Mean $0\cdot005065$

Reaction in Dark at 16°.

TABLE IV.

Time in minutes.	Conc. × 10⁴	k
0	49·00	...
20	39·00	0·011385
40	31·50	0·011017
60	26·00	0·010580
80	20·75	0·010143
100	16·50	0·010579
		Mean 0·010800

Reaction in Ordinary White Light at 6° and 16°

Intensity of incident energy = 19800 ergs per sq. cm. per sec. as measured by a Johansen thermopile and galvanometer calibrated with a Hefner lamp.

TABLE V.

Temperature 6°.

Time in minutes.	Conc. × 10⁴ mols.	k
0	43·25	...
10	35·00	0·02114
20	28·75	0·02038
30	23·25	0·02065
40	19·00	0·02054
		Mean 0·02068

TABLE VI.

Temperature 16°.

Time in minutes.	Conc. × 10⁴ mols	
0	43·50	
5	37·25	0·03100
10	32·00	0·03068
15	27·00	0·03174
20	23·25	0·03128
25	20·00	0·03105
		Mean 0·03115

It will be seen from Tables III and V that at 6° the velocity of reaction in light is exactly about four times the velocity in dark.

Effect due to Light only.

k in light — k in dark = $0·02068 - 0·00506 = 0·01562$ at 6° ; or = $0·03115 - 0·01080 = 0·02035$ at 16°.

Temperature coefficient between 6° and 16° of velocity of reaction in light = $\dfrac{0·02035}{0·01562}$ = $1·30$.

Temperature coefficient of velocity of reaction in dark.

$$= \frac{0·01080}{0·00506} = 2·13.$$

It was found that the concentration of potassium oxalate when varied between N and $N/10$ had no perceptible influence on the velocity of the decomposition.

Reaction in Plane and Circularly Polarised Lights.

Intensities of light in these three cases were adjusted by using lenses of suitable foci, so that they were almost equal to one another and equal to that of ordinary white light employed in the experiments above.

TABLE VII.

Temperature 6°.

Intensity.	Kind of light.	k
19300 ergs. per sq cm. per sec.	Ordinary	0·02038
19620 ,, ,, ,,	Plain polarised	0·02088
20070 ,, ,, ,	Circularly polarised.	0·02254

It will be seen from the above table that the velocity of photo-decomposition in ordinary and plane polarised white light is the same, but circularly polarised light has a slightly greater efficiency.

Effect of Adding Oxalic Acid to the Reaction Mixture on the Velocity of Decomposition.

Two series of measurements were made by adding 0·2 g. and 2·0 g. of oxalic acid to a litre of normal potassium oxalate solution. The following table gives the results obtained at 6° in darkness and in light.

TABLE VIII.

0·2 g. of oxalic acid per litre.

Intensity.	Kind of light.	k
..	In darkness	0·004577
19800 ergs per sq. cm. sec^{-1}.	Ordinary light	0·020079
19620 ,, ,,	Plane polarised light	0·020930
20070 ,, ,,	Circularly polarised light	0·023437

TABLE VIII—*Continued.*

2·0 g. of oxalic acid per litre.

	In darkness	0·00358
19800 ergs per sq. cm. sec⁻¹	Ordinary light	0·015249
19620	Plane polarised light	0·015856
20070	Circularly polarised light	0·016774

The effect of adding oxalic acid is thus to depress the velocity of decomposition both in darkness and in light. Otherwise the results are similar to those obtained in neutral potassium oxalate solution.

Temperature Coefficient of Velocity of Decomposition in Darkness and in Light.

TABLE IX.

0·2 g. of oxalic acid per litre.

Temp.	Velocity constant	Temp. coeff. per 10°
6°	In darkness—0·004577	
16°	In darkness—0·009563	2·06
6°	In light—0·03007	
16°	In light—0·02974	
6°	(k in light$-k$ in dark)$=0·01550$	
16°	(k in light$-k$ in dark)$=0·02028$	

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Table IX.—*Continued.*

2 g. of oxalic acid per litre.

Temp.	Velocity constant.	Temp. coeff. per 10°
6°	In darkness —0·003588 ⎫	
16°	In darkness —0·01136 ⎭	3·16
26°	In darkness —0·03767	3·30
6°	In light —0·01242	
16°	In light —0·02341	
26°	In light —0·05748	
6°	(k in light —k in dark) —0·00883	
16°	(k in light —k in dark) —0·01205 ⎫	1·36
26°	(k in light —k in dark) —C·01979 ⎭	1·64

The temperature coefficient for the dark reaction in al these cases is very large ranging from 2·06 in neutral oxalate solution to 3·30 in oxalate solution containing 2·0 g. of oxalic acid per litre. The temparature coefficient for the velocity of photochemical decomposition on the other hand is quite small, near about 1·3. This is in conformity with other experimental data in this field and is to be expected.

Influence of Intensity of Incident Light on the Velocity of Photochemical Decomposition:

M/200 of manganic acetate dissolved in *N*-potassium oxalate containing 2 g. of oxalic acid per litre was used in the three following experiments.

TABLE X.,

Intensity of light.	k in light.	(k in light — k in dark)
16100 ergs.cm² sec⁻¹	0·01242	0·00883
19800 ,,	0·01525	0·01166
24300 ,,	0·02049	0·01681

The velocity as is to be expected increases with increase in the intensity of the incident light but there is no simple relation between the velocity constant and the intensity of *incident* radiation. In order, however, to determine the relation between the quantity of chemical transformation and the energy of the light, the quantity of light absorbed must be measured and this measurement is described in the next section.

Velocity of Photochemical Decomposition in approximately Monochromatic Light of Wave-length 488μμ.

To obtain an approximately monochromatic radiation of wave-length 488μμ Plotnikow (*Photochemische Versuchtechnik*, p. 59) recommends the use of two filters, one a solution of Doppelgrün SF (0·02%) and another of $CuSO_4 \cdot 5H_2O \cdot (15\%)$ each of a thickness of 20 mm. to be used together. These filters were employed with white light in the following experiments (M/200 manganic acetate dissolved in neutral *N*-potassium oxalate solution was used):

TABLE XI.

Intensity of blue light 6075 ergs per cm² per sec.
Temperature 6°.

Time in minutes.	Conc. × 10⁴	Velocity constant.
0	48·2	...
10	39·00	0·02114
20	31·75	0·02003
30	28·00	0·01808
40	24·00	0·01741
50	20·50	0·01707
60	17·20	0·01714

TABLE XII.

Intensity of blue light 2295 ergs per cm² per sec.
Temperature 6°.

Time in minutes.	Conc. × 10⁴	Velocity constant
0	47·75	...
10	43·25	0·00989
20	39·25	0·00980
30	36·00	0·00941
45	32·50	0·00855
60	29·50	0·00803
75	26·50	0·00784

The velocity of decomposition in dark is 0·005083. It will be noticed from Tables XI and XII that the velocity of decomposition in blue light is roughly proportional to the intensity of incident radiation; but the velocity constants fall as decomposition progresses.

Polarised Light.

Experiments carried on in plane polarised and circularly polarised light with the colour filters, used in the above two experiments and with an incident of radiation $=6075$ ergs per sq. cm. per sec. gave almost identical results with those given in Table XI.

Application of Einstein's Law of Photochemical Equivalence.

This law is strictly applicable to monochromatic radiation. In the present investigation the reaction for obvious experimental difficulties could not be carried on in monochromatic light, but the use of filters mentioned above gave a beam which approximated in quality to monochromatic radiation.

From the first two readings in Table XI we find that $9 \cdot 2 \times 10^{-7}$ gm. mols are decomposed in 600 seconds, per litre. Therefore the actual number of molecules decomposed per c.c. per sec.

$$\frac{9 \cdot 2 \times 10^{-7} \times 6 \cdot 1 \times 10^{23}}{600} = 9 \cdot 3 \times 10^{14}.$$

The number of molecules decomposed per sq. cm. of the surface under the influence of radiation in the reaction cell $= 9 \cdot 3 \times 10^{14} \times 1 \cdot 65$ ($1 \cdot 65$ being the thickness of the reaction cell). Of these 1/4th the number of molecules are decomposed by thermal energy alone, so that the number of moleculs decomposed photochemically

$$= \frac{9 \cdot 3 \times 10^{14} \times 1 \cdot 65 \times 3}{4} = 11 \cdot 5 \times 10^{14} \text{ mol.}$$

It was found that with the light source and experimental arrangement used, the intensity of the transmitted blue light through the reaction cell filled with only potassium oxalate solution was equal to 5175 ergs cm^2 sec^{-1} while the intensity of the beam with the cell filled with

potassium oxalate solution in which manganic acetate was dissolved (concentration of the manganic salt being equal to 45×10^{-4}M, about the average concentration between 48 and 39×10^{-4}M) was equal to 1575 ergs per sq. cm. per sec. The energy absorbed in passing through the thickness of solution in the cell per sq. cm. per sec. is therefore the differerence of these quantities *viz.*, $5175 - 1575 = 3600$ ergs cm^{-2} sec^{-1}. One quantum of blue light

$$= \frac{hc}{\lambda} = \frac{6 \cdot 55 \times 10^{-27} \times 3 \times 10^{10}}{488 \times 10^{-7}},$$

The number of quanta of light absorbed by the decomposing substance is therefore equal to

$$\frac{3600 \times 488 \times 10^{-7}}{6 \cdot 55 \times 10^{-27} \times 3 \times 10^{10}} = 8 \cdot 94 \times 10^{14}$$

Therefore the number of molecules decomposed per quantum of energy absorbed

$$= \frac{11 \cdot 5 \times 10^{14}}{8 \cdot 94 \times 10^{14}} = 1 \cdot 28$$

or roughly one quantam transforms one molecule. It is clear therefore that in this case the law of Einstein is quite applicable. The fact that the temperature co-efficient of the velocity of photochemical decomposition is just a little above unity lends additional support to this conclusion.

Our thanks are due to Mr. Sailendra Nath Sen who carried out a large number of preliminary experiments in this connection.

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The Essential Oil from the Flowerheads of *Perovskia Atriplicifolia,* Benth.

BY

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The essential oil from *Perovskia atriplicifolia*, Benth, does not appear to have been examined before. *P. atriplicifolia* occurs in Western Tibet, in Afghanistan and Baluchistan at altitudes of 7,500 to 10,200 feet (Hooker's *Flora*). The samples used were kindly sent by the Political Agent, Kurram, Parachinar, N. W. F. Province and were identified by Mr. R. N. Parker, the Forest Botanist of this Institute.

The samples were distilled on a semi-large scale at this Institute. Only flowerheads were used; these were steam distilled at a pressure of 40 lbs. and a dark green oil with a strong camphoraceous odour was obtained. The yield of oil was 1·0 per cent. on the weight of air-dried flowerheads. Stalks were found to give a similar oil but the yield of oil was only 0·2 per cent.

When the oil had been dried by anhydrous magnesium sulphate and filtered, it had a light olive-green

colour, and had the following constants: d^{30}_{30} 0·8943; n^{30}_D ·1·4748; $[a]^{30}_D$ +8·53°, acid value 0·2; ester value, 30·4; ester value, after acetylation, 49·22. These values for ester, before and after acetylation, appear to indicate an ester content of 10·8 per cent. and of free alcohol 5·4 per cent. in the oil.

A preliminary examination of the oil showed that it was free from aldehydes and ketones and that it consists of about 50 per cent. of terpenes among which d-a-pinene, β-pinene and camphene have been definitely identified, 15-18 per cent. of alcohols and esters consisting mainly of d-borneol and bornyl acetate, and the rest of sesquiterpenes consisting mainly of a-caryophyllone and aromadendrene. The combined acids were found to consist almost entirely of acetic acid, no other acids having been discovered. Tests for cineol have so far given negative results although the higher fractions among the terpene fraction have a very strong odour of eucalyptus.

As a source of d-borneol this oil would seem to be of interest, and of some economic importance, particularly in view of the fact that camphene is also present in the oil; but this will largely depend on the quantity of material available. The necessary data regarding the occurrence and maximum output of the flowerheads of *F. atriplicifolia* are not within the scope of this paper. d-Borneol has been known to occur in the oil of the Borneo camphor tree (Schimmel's Report, 1913, 33), and in *Callitris calcarata* and *C. Glauca* (Baker and Smith, *A Research on the Pines of Australia*).

Systematic repeated fractionations of the bulk oil at 200 mm. pressure using a four pear still-head gave the following fractions:—

Fraction	B. p.	Yield.	Sp. gravity.	Ref. index.	Rotation.	Analysis C	H
I	120-125°	4·8 per cent.	0·8604	1·4611	+11·16	88·0	11·9
II	125-130°	20·0 per cent.	0·8683	1·4630	+12·93	87·7	11·9
III	130-135°	7·1 per cent.	0·8756	1·4634·	+15·45	85·1	11·2
IV	135-140°	8·2 per cent.	0·8802	1·4640	+17·66	83·2	11·5
V	140-145°	8·0 per cent.	0·9072	1·4640	+20·01	81·3	11·3
		47·6 per cent.					
VI	155-160°	2·0 per cent.					
VII	165-175°	10·2 per cent.	0·9383	1·4705	+10·95	75·2	10·5
VIII	175-185°	2·5 per cent.					
IX	185-190°	1·8 per cent.					
		16·5 per cent.					
X	200-210°	6·5 per cent.	0·9078	1·4970	−1·06	87·7	11·8
XI	210-220°	21·7 per cent.	0·9221	1·5012	+1·02	87·9	11·8
		28·2 per cent					

(The use of the fourpear still-head was discontinued while distilling fractions above 190°).

Fractions I-V consisted mainly of the terpenes : Fraction I had the familiar smell of pinene and fractions IV and V had the strong smell of cineol. As the density of all these fractions was high, they were suspected to contain traces of borneol or bornyl acetate, and were therefore refractionated over sodium at the ordinary pressure of 700 mm. The following new fractions were thus obtained.

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Fraction	B. p.	Yield.	Sp. gr.	Ref. index.	Rotation.	Analysis	
						C	H
I	154-156°	1·1 per cent.	0·8580	1·4620	+12·31	88·2	11·8
II	156-160°	5·2 per cent.	0·8606	1·4625	+12·9	87·8	11·9
III	160-164°	6·7 per cent.	0·8646	1·4629	+87·9	11·8	
IV	164-168°	6·2 per cent.	0·8688	1·4630	+15·0	87·5	11·8
V	168-172°	8·5 per cent.	0·8734	1·4630	+16·9	85·0	11·3
VI	172-180°	3·0 per cent.	0·8750	1·4640	+15·3		

Fraction I consists mainly of d-a-pinene, which gives a good yield of the nitrosochloride; this when recrystallised from cold chloroform and methyl alcohol crystallised in fine white needles m. p. 109° (with decomposition). The nitrol piperidine crystallised from dilute alcohol, m. p. 118°. Pinene nitrosochloride was obtained from fractions II and III so that these fractions also contained a-pinene. β-Pinene and camphene were absent in fraction I. Fraction II consists of d-a-pinene, camphene and a, little β-pinene. Camphene was identified by hydrating this fraction with acetic acid – sulphuric acid solution and hydrolysing the oil so obtained with alcoholic potash. iso-Borneol, b. p. 210-215°/700 mm., was obtained. This when recrystallised from light petroleum crystallised in snow white flakes m. p. 209-210° (in sealed tube). β-Pinene was identified by oxidising fraction II with dilute ice-cold permanganate in caustic soda solution and working up the oxidation products in the usual manner, when a little sparingly soluble sodium salt of nopinic acid was obtained, from which on acidifying and extracting with benzene, nopinic acid crystallising in prismatic needles were obtained. These when recrystallised from hot water gave the pure acid m. p. 126-127.° A mixture with nopinic acid made from pure pinene was unaltered in melting point.

Fraction III consists mainly of β-pinene, a little camphene and a little pinene. This fraction gave a good yield of nopinic acid.

Fraction IV. contains β-pinene mainly, camphene being absent. Fraction V and VI had a strong smell of cineol but these fractions gave no phosphoric acid compound. Tests for limonene were negative. Phellandrene is possible as a small trace of a nitrosite was obtained. These fractions are still under examination.

Fraction VII on distilling gave a small quantity of d-borneol (1·0 per cent.). Fractions ·VI to IX consisted of esters and alcohols. These were mixed together and saponified with alcoholic potash and the alcohol so obtained was repeatedly fractionated, the borneol fractions being congealed in ice and rapidly filtered each time. In this manner 8·5 per cent. of d-borneol was obtained. This was found to be free from camphor, as on treating its alcoholic solution with aqueous solution of semicarbazide acetate, no semicarbazone was obtained.

d-Borneol b. p. 210°/700 mm. had the following constants when crystallised from light petroleum : m. p. 200-201°; Sp. gr., 1·008 : rotation ·in alcohol, $+34·5°$; analysis, C=78·0; H=11·8.

After separation of the d-borneol from the fraction of b. p. 200-220°/700 mm. the saponified oil gave the following fractions :

Fraction.	B. p.	Yield.	Sp. gr.	Ref. index.	Rotation.
(A)	170-180°/700 mm.	4·3 per cent.	0·8760	1·4640	+15·8
(B)	180-185° ,,	1·0 ,,	—	1·4658	+15·0
(C)	185-195° ,,	1·2 ,,	0·9282	1·4670	——
(D)	200-220° ,,	3·0 ,,	0·9303	1·4730	+13·4

These alcohols are still under examination. Fraction (A) from its constants would appear to be mainly a hydrocarbon.

Fractions X and XI were found to consist mainly of sesquiterpenes. These were fractionated over sodium and the following main fractions were obtained:

Fraction	B. p.	Yield (per cent.)	Sp. gr.	Ref. index.	Rotation.	Analysis.	
						C	H
(a)	125-130°/5 mm. or 255-260°/700 mm.	16·6	0·9078	1·4970	−1·06	87·8	11·8
(b)	130-135°/5 mm or 260-262°/700 mm.	4·1	0·9109	1·4978	−0·76	88·1	11·8

No sesquiterpene alcohol was present. Both these sesquiterpene fractions gave all the colour reactions of aromadendrene (Baker and Smith, "A Research on the Eucalyptus and their Essential Oils," p. 416). Thus an acetic acid solution or a chloroform solution of the oil gave a purple colour when a very dilute solution of bromine in acetic acid was added : this purple colour developes to an indigo blue. Phosphoric acid also gave a light crimson colour, so did concentrated hydrochloric acid or sulphuric acid when each of these was added separately to the acetic acid solution or chloroform solution of the sesquiterpene. Colour reactions for cadinene were negative. α-Caryophyllene was identified in both the above fractions, as they each gave a fair yield of nitrosochloride, m. p. 164-165.° This when recrystallised from cold chloroform and methyl alcohol gave prisms m. p. 179° (with decomp.). The corresponding nitrol piperide crystallises from alcohol, m. p. 145° (Wallach and Tuttle quote m. p. 143° for α-caryophyllene nitrol piperide). The other derivatives of α-caryophyllene are being prepared for confirmation.

The combined acids were found to consist only of acetic acid. The alkaline solution obtained from the saponification of the esters was rendered free of oil and acidified with dilute sulphuric acid and steam distilled and the distillate was collected in fractions.

Fraction I. 0·3347 Ag-salt gave Ag = 0·2166.

Found : Ag = 64·73 per cent.

Fraction II. 0·2784 Ag-salt gave Ag = 0·1762.

Found : Ag = 63·3 per cent.

Fraction III. 0·4114 Ag-salt gave Ag = 0·2661.

Found : Ag = 64·7 per cent.

CH_3COOAg requires Ag = 64·6 per cent.

No other acids, either volatile or non-volatile in steam, could be detected.

The author wishes to take this opportunity to thank the Political Agent, Kurram, Parachinar, N. W. F. Province for the supply of the flowerheads, and to Mr. A. Rodger, O. B. E., President, Forest Research Institute for permission to publish these results and for his keen interest in the work.

Thiodiazines. Part III. Hydroxythiodiazines.

By

Prafulla Kumar Bose.

In continuation of the investigation of $1 : 3 : 4$-thiodiazines it has been found that certain a-halogenated esters of aliphatic acids condense with benzyl- or nitrobenzyl-dithiocarbazinates which contain the skeleton $NH_2 \cdot N = C(SH)$-, necessary for the synthesis of the $1 : 3 : 4$-thiodiazine ring-system (*cf.* this *Journal*, 1924, *1*, 53; *ibid*, 1925, *2*, 95). The condensation, which is best carried out in alcoholic solution in presence of pyridine or the calculated quantity of ammonia, hardly takes place in absence of these condensing agents; which evidently act by eliminating hydrobromic acid.

$$NH_2 \cdot N = C(SH) \cdot SCH_2Ph + EtO \cdot CO \cdot CHR \cdot Br$$

$$(I)$$
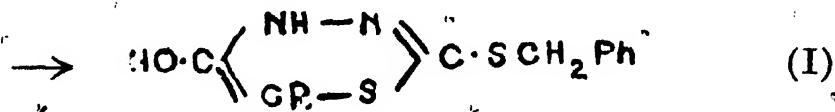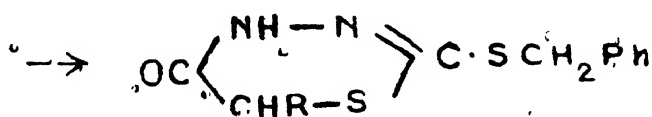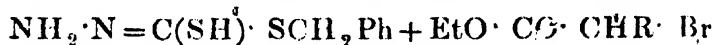
Condensation of benzyldithiocarbazinate with a-bromo-*iso*butyric and a-bromo-n-butyric esters, however, did not take place even when these substances were boiled with alcoholic ammonia.

The thiodiazines obtained are well-defined crystalline bodies, neutral to litmus but soluble in cold alkali : they are precipitated from the alkaline solution by mineral

acids as should be expected from the hydroxylic structure (I) given above,

An attempt was made to obtain 2-thiol-5-hydroxy-1 : 3 : 4-thiodiazine (II) by the condensation of potassium dithiocarbazinate and monochloroacetic ester, thus :

$$NH_2 \cdot N = C(SH) \cdot SK + Cl \cdot CH_2 \cdot CO \cdot OEt$$

$$\longrightarrow \quad CO \Big\langle {}^{NH-N}_{CH_2-S} \Big\rangle C \cdot SH$$

$$\longrightarrow \quad HO \cdot C \Big\langle {}^{NH-N}_{CH-S} \Big\rangle C \cdot SH \quad (II)$$
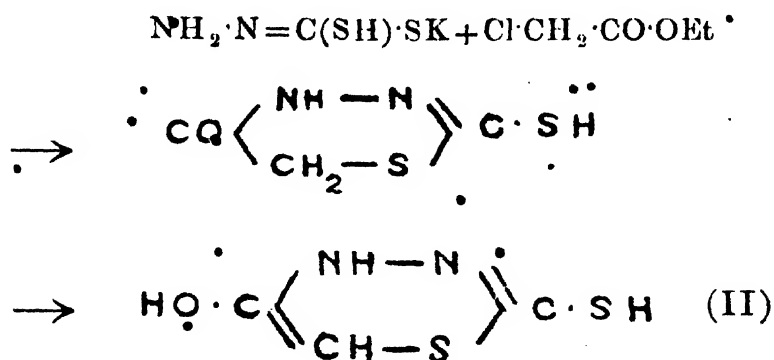
The reaction, doubtless, takes place in an alcoholic solution of the components at the ordinary temperature; but the isolation of the mercaptan from the reaction mixture in a pure condition proved unsuccessful. The disulphide of (II) was, however, easily obtained on keeping the reaction mixture exposed to air for several hours. An attempt to reduce this compound to the mercaptan (II) was unsuccesful.

When chloroacetic acid is added to a solution of potassium dithiocarbazinate the principal product of reaction is 2-thiol -1 : 3 : 4-thiodiazole-5-thiolacetic acid.

$$\begin{array}{c} N-N \\ \| \quad \| \\ HS \cdot C \quad C \cdot S \cdot CH_2 COOH \\ \diagdown \; \diagup \\ S \end{array}$$
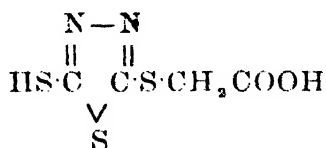
The formation of this compound is interesting in view of the fact that methods for obtaining it from 2 : 5-dithiol-1 : 3 : 4-thiodiazole and chloroacetic acid have been fruitless (Rây, Guha and Das, *J. Chem. Soc.*, 1919, **115**, 1309).

EXPERIMENTAL

2-*Thiobenzyl-5-hydroxy*-1 : 3 : 4-*thiodiazine*.

One mol. of benzyldithiocarbazinate (Busch, *J. pr. Chem.*, 1916, [ii] *93*, 25), which is best crystallised from hot xylene, was dissolved in warm alcohol, slightly more than one mol. of monochloro acetic ester added and then one mol. of alcoholic ammonia was run in with constant shaking. Reaction took place with rise of -temperature and within a few minutes crystals of ammonium chloride began to separate. After an hour the product was diluted with water when a reddish brown oil was precipitated which solidified. This was collected, dried on porous porcelain, dissolved in cold benzene and filtered. The filtrate was diluted with ligroin when colourless rhombic plates of 2-*thiobenzyl-5-hydroxy*-1 : 3 : 4-*thiodiazine* were obtained. After recrystallisation from a mixture of benzene and ligroin it melted at 123-24°. The yield was quantitative. The ammonia can be replaced by pyridine, but in this case, in order to ensure complete reaction, it was found necessary to heat the mixture under reflux for 15 to 20 minutes. (Found : N=11·94. $C_{10}H_{10}ON_2S_2$ requires N=11·77 por cent.).

It is easily soluble in alcohol, benzene, ether, pyridine and acetic acid, insoluble in ligroin. On adding warm caustic soda (8-9 per cent.) it dissolves and on cooling the solution deposits beautiful slender needles of the *sodium salt* which is hygroscopic and very soluble in alcohol or acetone. On benzoylation of the compound by the Schotten-Baumann method a yellow semi-solid mass was obtained. It solidified on cooling below 0° and was insoluble in alkali and very soluble in most organic solvents. It slowly decomposed in presence of water or alkali and therefore could not be obtained pure for analysis. Benzoylation in pyridine solution gave no better result.

2-Thiobenzyl-5-methoxy-1 : 3 : 4-thiodiazine.—Molecular proportions of 2-thiobenzyl-5-hydroxy-1 : 3 : 4-thiodiazine, caustic soda (5 per cent. aqueous solution) and methyl iodide were heated together on the water-bath under reflux until the methyl iodide had disappeared. The resulting oil was extracted using ether, the ethereal solution was shaken with dilute caustic soda solution to remove any unchanged hydroxythiodiazine, washed several times with water, and dried by calcium chloride. The ether was removed under reduced pressure. Obtained in this manner, the methoxy derivative formed a thick, pale brown oil with a peculiar strong odour. (Found: $C = 52 \cdot 10$; $H = 5 \cdot 06$. $C_{11}H_{12}ON_2S_2$ requires $C = 52 \cdot 38$; $H = 4 \cdot 76$ per cent.)

o-Nitrobenzyl dithiocarbazinate.—The method of preparation is practically the same as given by Busch for the benzyl derivative (*loc. cit.*). Hydrazine hydrate (5 g.) and a 10 per cent. alcoholic solution of caustic potash (56 c.c.) were mixed and the mixture was cooled to $0°$. Carbon disulphide ($7 \cdot 6$ g.) was gradually run in so that the temperature of the reaction mixture did not rise above $25°$. *o*-Nitrobenzylchloride (12 g.) was then added and the mixture shaken at the room temperature for about an hour, the temperature of the reaction mixture being not allowed to rise above $50°$. On adding water to the reaction mixture an oil was precipitated which solidified on cooling. From benzene it separated in pale-yellow glistening plates which melted at $94°$ after shrinking at $92°$. It was easily soluble in alcohol, acetone, hot benzene or aqueous alkalis but almost insoluble in ligroin. (Found: $S = 26 \cdot 74$. $C_8H_9O_2S_2N_3$ requires $S = 26 \cdot 37$ per cent.).

2-Thio-o-nitrobenzyl-5-hydroxy-1 : 3 : 4-thiodiazine, from ethyl chloracetate and *o*-nitrobenzyl dithiocarbazinate, formed transparent needles melting at $151°$. It

was sparingly soluble in benzene and alcohol but could be easily crystallised from acetone and water. (Found: N=14·97. $C_{10}H_9O_3N_3S_2$ requires N=14·84 per cent.).

2-*Thio*-p-*nitrobenzyl*-5-*hydroxy*-1 : 3 : 4-*thiodiazine* was obtained from *p*-nitrobenzyldithiocarbazinate and ethyl chloroacetate in quantitative yield. It was sparingly soluble in alcohol or benzene but easily dissolved in pyridine or acetone. From a mixture of acetone and benzene it was obtained as long, white, slender needles melting at 173°. (Found: N=14·96. $C_{10}H_9O_3N_3S_2$ requires N= 14·84 per cent.).

2-*Thiobenzyl*-5-*hydroxy*-6-*methyl*-1 : 3 : 4-*thiodiazine* was obtained from α-bromopropionic ester and benzyldithiocarbazinate. It separated from a mixture of benzene and ligroin in colourless crystals which melted at 110-111°. (Found: N=11·21. $C_{11}H_{12}ON_2S_2$ requires N= 11·11 per cent.).

2-*Thiobenzyl*-5-*hydroxy*-6-*carbethoxy*-1 : 3 : 4-*thiodiazine*.—Molecular proportions of benzyl dithiocarbazinate, bromomalonic ester and alcoholic ammonia were heated together on the water-bath for a few minutes and allowed to stand for several hours. On adding water to the product an oil separated which partly solidified after some time. This was collected and pressed on porous plate : it crystallised from benzene after treatment with animal charcoal in colourless needles melting at 116-117°. (Found: N=9·14. $C_{11}H_{10}O_3N_2S_2$ requires N=9·03 per cent.).

2-*Thiol*-5-*hydroxy*-1 : 3 : 4-*thiodiazine*-*disulphide*—Hydrazine hydrate (100 per cent., 5 g.) was added to a solution of caustic potash (5·6 g.) dissolved in alcohol (60 c.c.). The mixture was cooled to 0°, carbon bisulphide (7·6 g.) was gradually added when a straw-colored oil separated out. Ethyl chloroacetate (11·5 g.) was then

poured into the mixture which was thoroughly shaken for a few minutes and kept at the ordinary temperature for about 2 hours. The precipitated potassium chloride was removed, and the filtrate was exposed to air. The crystalline residue, which contained some ethyl chloroacetate and other oily impurities, was dried on porous plate and twice recrystallised from hot benzene or alcohol from which it separated in pale yellow, ferny crystals melting at 92°. The yield of the *disulphide* of 2-*thiol*-5-*hydroxy*-1 : 3 : 4•*thiodiazine* was about 45 per cent. (Found: N = 18·89; S = 43·30. $C_6H_6O_2N_4S_4$ requires N = 18·92; S = 43·51 per cent.).

It was a fairly strong acid and decomposed sodium bicarbonate in the cold. It gave a pale yellow precipitate with mercuric chloride but not with lead acetate ; it scarcely decolorised a solution of iodine. It was soluble in hot water, insoluble in light petroleum but very soluble in pyridine, acetone and glacial acetic acid.

Reduction of the Disulphide.—The disulphide, dissolved in sodium carbonate solution, was reduced by means of the •aluminium-mercury couple. The reduction product was isolated as a lead salt, and was ultimately obtained as a brown viscous oil. Analysis showed that it was not the desired substance.

2-Thiol-1 : 3 : 4-*thiodiazole-5-thiolacetic Acid.*—A mixture of 5·6 gms. of caustic potash (10 per cent. in alcohol) and 5 gms. of hydrazine hydrate (100 per cent.) was cooled with ice and to the mixture were gradually added 7·6 g. of carbon disulphide and finally 8·5 g. of chloroacetic acid. The mixture was well-shaken and allowed to stand for about two hours at the ordinary temperature during which period evolution of H_2S was noticed. The mixture of potassium chloride and the *potassium salt* of 2-thiol-1 : 3 : 4-thiodiazolo-5-thiolacetic acid, which had separated, was collected and crystallised from hot water

to remove potassium chloride. The potassium salt was dried and extracted with hot benzene to remove a small quantity of the disulphide (*vide supra*) and the residue twice crystallised from hot water containing a little alcohol when long, silky needles melting and decomposing at 252-53° were obtained (6 g.). The potassium salt contains one mol. of water of crystallisation. (Found: $K = 14·63$; $S = 36·45$; loss of water at $130° = 7·00$. $C_4H_3O_2S_3N_2K$, H_2O requires $K = 14·78$; $S = 36·00$; $H_2O = 6·82$ per cent.). It was easily soluble in hot water but insoluble in most organic media.

The free mercaptan, 2-*thiol*-1 : 3 : 4-*thiodiazole*-5-*thiolacetic acid* was obtained by acidifying an aqueous solution of the potassium salt with hydrochloric acid. It crystallised from hot water in pale yellow, glistening plates melting at 164°. It was very soluble in alcohol, ether, acetone or glacial acetic acid and insoluble in benzene or ligroin. (Found: $S = 46·85$; $N = 13·25$. $C_4H_4O_2N_2S_3$ requires $S = 46·15$; $N = 13·46$ per cent.).

The aqueous solution of the mercaptan on being treated with iodine solution gave a crystalline precipitate of the *disulphide* which separated from a large quantity of alcohol in microscopic needles melting and decomposing at 180°. It possessed acidic properties. (Found: $N = 13·56$. $(C_4H_3O_2N_2S_3)_2$ requires $N = 13·53$ per cent.).

My best thanks are due to Sir P. C. RâY who has taken a keen interest in the progress of the investigation.

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Varying Valency of Platinum with respect to Mercaptanic Radicles.

Part III.

BY

PRAFULLA CHANDRA RÂY, BIRKS CHANDRA GUHA

AND

KSHITISH CHANDRA BOSE-RÂY.

The remarkable complex compounds derived from platinic chloride and ethyl sulphide, which have been described in a foregoing communication (this *Journal*, 1925, 2, 178), have now been subjected to treatment with ammonia and organic bases. The results obtained have thrown considerable light on their constitutions (*loc. cit.*). The products formed are well-known compounds of the Werner type. The evidence is, therefore, directly corroborative of the Werner constitution of the compounds studied, as already suggested.

In the present paper the action of ammonia and pyridine on some of the isomeric varieties of $PtCl_2$, $2Et_2S$ and on $PtCl_3$, $2Et_2S$ and $PtCl_4$, $2Et_2S$ has been studied.

Action of Ammonia and Pyridine on $PtCl_2$, $2Et_2S$.

By the action of ammonia $PtCl_2$, $2Et_2S$ is converted into $PtCl_2$, $4NH_3$; $2Et_2S$ is thus replaced by $4NH_3$. This may be most conveniently represented on the Werner model as follows :—

$$\left[\begin{array}{c} Cl \\ Cl \end{array} \!\!>\!\! \underset{Pt}{\overset{II}{}} \!\!<\!\! \begin{array}{c} Et_2S \\ Et_2S \end{array} \right] \xrightarrow{4NH_3} \left[\begin{array}{c} NH_3 \\ NH_3 \end{array} \!\!>\!\! \underset{Pt}{\overset{II}{}} \!\!<\!\! \begin{array}{c} NH_3 \\ NH_3 \end{array} \right] Cl_2$$

Cl non-ionisable   Cl ionisable
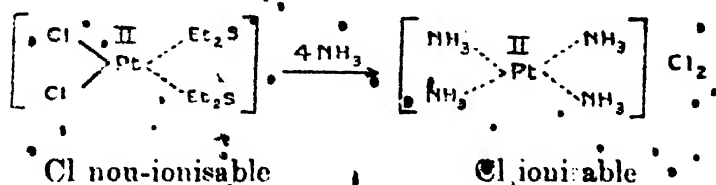
Almost all the modifications of $PtCl_2$, $2Et_2S$ gave a

white compound of the composition $PtCl_2$, $4NH_3$, soluble in water. It was identical in each case. All the products were found to give chlorine ions in aqueous solution as expected from theory. It will be noticed that Blomstrand's *cis*-and *trans*-modifications of $PtCl_2$, $2Et_2S$ (*loc. cit.*) are converted into one and the same compound by treatment with ammonia. If a compound of the constitution $Pt(Et_2S)_4PtCl_4$ (*loc. cit.*) were existing as one of the isomerides of $PtCl_2$, $2Et_2S$, then a compound, identical with Magnus' salt in composition $Pt(NH_3)_4 PtCl_4$ would be expected to be formed by treatment with ammonia. But so far no such compound has been isolated from the modifications studied.

The action of pyridine on one of the modifications of $PtCl_2$, $2Et_2S$ has been studied, namely, on the compound of m.p. $77°$. In this case, however, two compounds have been isolated, in which the two Et_2S residues are replaced by two and four molecules of pyridine respectively. The reaction may be represented on the Werner model, thus:

$$\begin{bmatrix} Py & & Py \\ & >Pt< & \\ Py & & Py \end{bmatrix} Cl_2 \xleftarrow{4 Py} \begin{bmatrix} Cl & II & Et_2S \\ & >Pt< & \\ Cl & & Et_2S \end{bmatrix} \xrightarrow{2 Py} \begin{bmatrix} Cl & II & Py \\ & >Pt< & \\ Cl & & Py \end{bmatrix}$$

$$\text{I} \qquad\qquad\qquad\qquad\qquad\qquad \text{II}$$
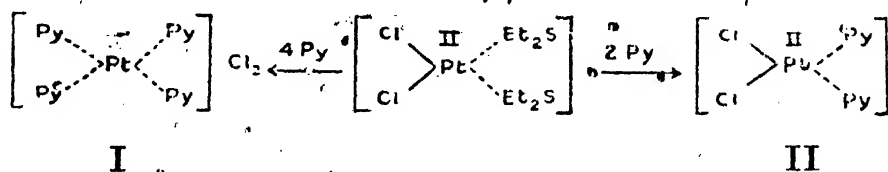
Compound (II) was found to be insoluble in water, while compound (I) was very soluble in water, evidently because it is an ionisable chloride.

Action of Ammonia on $PtCl_3$, $2Et_2S$.

In the paper of Rây and Bose-Rây (*loc. cit.*) the authors have given an experimental confirmation of the proposed constitution of the substance. When crystallised from boiling alcohol, the compound in question breaks up into $PtCl_2$, $2Et_2S$ and $PtCl_4$, $2Et_2S$, showing thereby that $PtCl_3$, $2Et_2S$ is a molecular compound of

the constitution $[(Et_2S)_2.PtCl_2].[(Et_2S)_2.PtCl_4]$. Further confirmation is now brought forward by studying the action of ammonia. From the resulting products a compound of the composition $PtCl_2, 4NH_3$ has been isolated, which has been evidently derived from the first component of the molecular compound depicted above. The product of the action of ammonia on the other component has not been isolated. The other proposed formula for this compound, viz., $[Pt(Et_2S)_4]PtCl_6$ (cf. Tschugaeff, *Zeit. anorg. Chem.*, 1913, 82, 420) might be expected to give a compound of the empirical composition $Pt(NH_3)_2Cl_3$, but no such compound has been so far isolated.

Action of Ammonia and Pyridine on $PtCl_4, 2Et_2S$.

Ammonia is found to give the compound $PtCl_4$, $4NH_3$ and pyridine the compound $PtCl_4, 2Py$, which readily lend themselves to interpretation on the Werner basis, thus :

III   IV
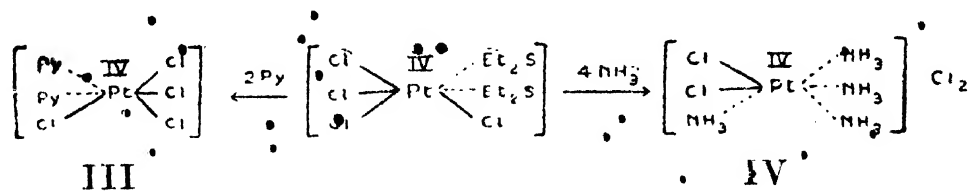
Compounds (III) and (IV) are well-known and can have no other constitutions than those suggested above. It is of interest to note here that these compounds, which had been obtained by previous workers direct from platinous chloride, etc., have now been obtained in quite a different way.

The replacement of Et_2S by ammonia and organic bases seems to occur step by step in at least some of the reactions of the above type (cf. Klason, *Ber.*, 1875, 28, 1496; *J. pr. Chem.* [2] 67, 33, 39 ; *Ber.*, 1904, 37, 1359 etc.). Some intermediate compounds of this variety will be described in a future communication.

The compounds $PtCl, Et_2S$ and $PtCl_5 (Et_2S)_2, 2H_2O$ are of uncertain constitution and are also under investigation.

EXPERIMENTAL.

Action of Ammonia on $PtCl_2, 2Et_2S$, m. p. 96°.

The compound was dissolved in a very small quantity of alcohol and an excess of alcoholic ammonia was added. The odour of ethyl sulphide was distinctly perceptible and in the course of some ten minutes the solution became colourless and white crystals began to separate out. After half-an-hour the first crop was filtered off, which being impure, was rejected. The filtrate on standing for three or four hours more deposited a second crop of colourless crystals, which were well washed with alcohol, dried between the folds of a filter-paper and kept for some time in a desiccator. (Found: $Pt = 58.68$; $Cl = 20.87$; $N = 15.28$. $PtCl_2, 4(NH_3)$, requires $Pt = 58.63$; $Cl = 21.13$; $N = 16.67$ per cent.).

Action of Ammonia on $PtCl_2, 2Et_2S$, m. p. 104°.

The compound was dissolved in a moderately large volume of alcohol and alcoholic ammonia was added. On standing for 6-7 hours long colourless needles crystallised out. These were washed with alcohol and dried in a desiccator. (Found: $Pt = 58.52$; $Cl = 21.36$; $N = 15.61$ per cent.).

Action of Ammonia on $PtCl_2, 2Et_2S$, m. p. 108°.

The compound was dissolved in benzene and dry ammonia gas passed into it so as to remove the ethyl sulphide from the sphere of reaction as soon as it was formed. The turbid solution was filtered and the filtrate spontaneously evaporated in a desiccator. The yellowish-white product was washed first with alcohol, then with

benzene (in both of which it is sparingly soluble) until the product was white and again finally it was washed with alcohol and then dried for 3 hours in a desiccator. (Found : Pt=59.79 Cl=21.55 per cent.)..

Action of Ammonia on $PtCl_2,2Et_2S$, m. p. 110°.

Gaseous ammonia was passed through an alcoholic solution of the compound when gradually colourless crystals came down which were filtered, washed with alcohol and dried. (Found : Cl = 22.37 per cent.).

Action of Pyridine on $PtCl_2, 2Et_2S$, m. p. 77°.

The compound was digested with a small quantity of pyridine on a water-bath for about half-an-hour until the whole thing went into solution. The solution on standing deposited small needles and on again warming the solution and standing a considerable quantity of yellow crystals came down. These were filtered, washed with a little pyridine and then with alcohol and dried in a vacuum desiccator. The compound shrinks at 260° and chars between 270° and 280.° It was crystallised from chloroform. It is practically insoluble in alcohol. (Found : Pt=46.37, 46.16; Cl=17.39; N=7.18. $PtCl_2$, $2C_5H_5N$ requires Pt = 46.24; Cl=16.66 and N=6.57 per cent.). The above platinum compound was also directly treated with pyridine in the cold. The compound dissolved and gradually a yellowish crystalline deposit was thrown down. After washing with a little pyridine and then with alcohol several times the substance melted at 175—76°. The mother-liquor, on being allowed to evaporate to dryness spontaneously, deposited fine white hexagonal plates which unlike the yellow compound were extremely soluble in water. (Found : Cl=11.58; N=9.32. $PtCl_2$, 4Py requires Cl=12.1; N=9.6 per cent.).

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Action of Ammonia on $PtCl_3, 2Et_2S$.—The substance was suspended in a very small quantity of water into which ammonia gas was passed. The compound slowly dissolved, giving finally a colourless solution. The solution was concentrated in a desiccator when colourless crystals separated out. These were filtered off, washed rapidly with very little water and dried for 4 hours in a desiccator. The filtrate on complete evaporation in a desiccator deposited another substance which, however, was brownish coloured and could not be sufficiently purified for analysis. (Found: $Pt = 58.68$; $Cl = 21.31$; $N = 17.09$. $PtCl_2, 4NH_3$ requires $Pt = 58.53$; $Cl = 21.13$ and $N = 16.67$ per cent.).

Action of Ammonia on $PtCl_4, 2Et_2S$.—The resulting compound was isolated in this case after several trials. Dry ammonia gas was passed for some 15 minutes into a benzene solution of the substance. The precipitate formed was filtered and washed with benzene and dried in a desiccator. (Found: $Pt = 48.13$; $Cl = 34.44$; $N = 16.68$. $PtCl_4, 4NH_3$ requires $Pt = 48.4$; $Cl = 34.9$; $N = 17.2$ per cent.).

Action of Pyridine on $PtCl_4, 2Et_2S$.—The compound was treated with a little pyridine and as it went into solution, yellow crystals began to separate out. After standing for 1-2 hours they were filtered, washed well with pyridine, alcohol, acetone and then dried in a vacuum desiccator. (Found: $Pt = 39.92$; $Cl = 28.06$; $N = 6.15$. $PtCl_4, 2C_5H_5N$ requires $Pt = 39.6$; $Cl = 28.5$ and $N = 5.6$ per cent.).

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Dyes derived from β-Phenyl-pyridine-dicarboxylic Acid.

By

Jamuna Datt Tewari and

Sikhibhushan Dutt.

In a previous paper by one of the present authors (Dutt, *J. Chem. Soc.*, 1923, *123*, 225) it was shown that diphenic anhydride condenses with aromatic amino and hydroxy compounds to form dyestuffs analogous to the phthaleins. In a previous paper by Ghosh (*J. Chem. Soc.*, 1919, *115*, 1102) it was shown that quinolinic anhydride condenses with aromatic amino and hydroxy compounds to form similar dyestuffs. From observations on these substances he concluded that the effect of nitrogen in the ring was to lighten the colour. But he did not measure the intensities of colour in the two series. Quantitative experiments on absorption spectra, which are now in progress in this laboratory, tend to show that the effect of the nitrogen atom in the ring is to intensify the colour instead of diminishing it. In order to obtain conclusive results further dyes have been prepared by condensing β-phenyl-pyridine-dicarboxylic acid with aromatic amino and hydroxy compounds, which are analogous in constitution to the dipheneins with the exception that they contain a nitrogen atom in the ring. These compounds are much more intense in colour than the corresponding dipheneins. The details of these quantitative experiments will be communicated later.

β-Pnenyl-pyridine-dicarboxylic acid condenses with aromatic amino and hydroxy compounds without the use of a condensing agent, but it has been found that by the use of a condensing agent the condensation is facilitated and the yield is better. The following substances have been made to condense with the dicarboxylic acid, and the corresponding dyestuff obtained :—phenol, resorcinol, catechol, phloroglucinol, hydroxy-quinol, m-phenylene diamine and diethyl-m-amidophenol. In general, properties these substances are similar to the corresponding dipheneins, but, as previously stated, the intensity of colour is greater.

EXPERIMENTAL.

Phenol-β-phenyl-pyridine-dicarboxylein.

$$\begin{array}{c} C_{11}\,H_7\,N \\ | \\ CO - O \end{array} \Big\rangle C \left(C_6\,H_4\,OH\right)_2$$
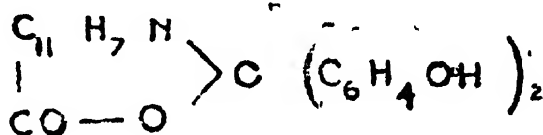
A mixture of β-phenyl-pyridine-dicarboxylic acid (1 mol.), phenol (2 mols. plus 20 per cent. excess), and stannic chloride (1 mol. plus 20 per cent. excess) was heated at 100·110° for 16 hours. The mixture was then poured into water and the excess of phenol distilled off in steam. The residue was extracted with dilute ammonia and the extract, after filtration, was acidified when the dye was precipitated as a colourless mass. It is a white crystalline substance which on keeping tends to assume a pale yellow colour. On heating it darkens at 250°, but does not melt even at 305°. The solution in alkali has a brilliant pink colour. (Found : C=76·03 ; H=4·39. $C_{25}H_{17}O_4N$ requires C = 75· 95 ; H = 4· 3 per cent.).

Resorcinol-β-phenyl-pyridine-dicarboxylein.

$$\begin{matrix} C_{11}H_7N \\ | \\ CO-O \end{matrix} \Big> C \Big< \begin{matrix} C_6H_3(OH) \\ C_6H_3(OH) \end{matrix} \Big> O$$
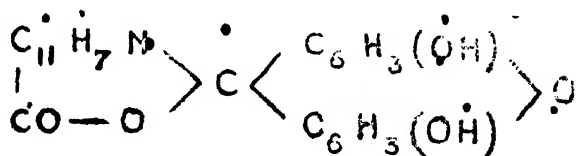
A mixture of β-phenyl-pyridine-dicarboxylic acid (1 mol.) and resorcinol (2 mols) was heated with a few drops of sulphuric acid at 180-200° for about an hour. The melt was extracted with alcohol and the alcoholic extract after filtration was diluted with water which caused the precipitation of the colouring matter in flocks. It was purified by precipitation from alkaline solution by dilute acid. It was thus obtained as a yellowish brown powder which sinters at 186° and melts with decomposition at 200°. The solution in alkali has an orange red colour and a light green fluorescence. (Found : C = 73·28; H = 4·2. $C_{25}H_{15}O_3N$ requires C = 73·34 ; H = 3·7 per cent).

Catechol-β-phenyl-pyridine-dicarboxylein.

A mixture of β-phenyl-pyridine-dicarboxylic acid (1 mol.), catechol (2 mols.) and stannic chloride (1 mol. plus 20 per cent. excess) was heated at 100-110° for about three hours. The melt was then poured into water and after through grinding the insoluble residue was washed with water. It was then extracted with alcohol and the alcoholic extract was diluted with water which caused the precipitation of the dyestuff as a crystalline powder. It is a colourless substance. The solution in alkali has a transient green colour. It does not melt at 310°. (Found : C = 73·6 ; H = 4·5. $C_{25}H_{15}O_3N$ requires C = 73·34 ; H = 3·7 per cent.).

Phloroglucinol-β-phenyl-pyridine-dicarboxylein.

$$C_{11}H_7N \atop CO-O \Big\rangle C \Big\langle {C_6H_2(OH)_2 \atop C_6H_2(OH)_2} \Big\rangle O$$
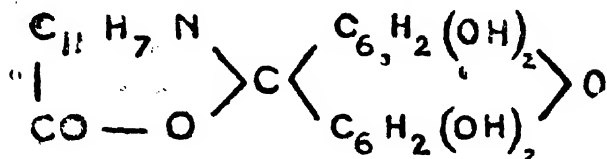
The condensation was effected as in the case of resorcinol with the difference that the temperature was kept at 150-170°. The product was isolated in a similar manner. It is a bright yellow crystalline powder which does not melt at 280°. The solution in alkali has an orange-red colour. (Found : C=67·2 ; H=3·2. $C_{25}H_{15}O_7N$ requires C=67·5 ; H = 3·3 per cent.).

Hydroxyquinol-β-phenyl-pyridine-dicarboxylein.

The condensation was effected as in the case of resorcinol and the substance was isolated in a similar manner. It is a light brown powder which melts with decomposition at 228-230°. The solution in alkali has a fine pink colour. (Found : C=68·5 ; H=4·09. $C_{25}H_{15}O_7N$ requires C=67· 5; H=3·3 per cent.).

m-*Diethyl-amidopherol-β-phenyl-pyridine-dicarboxylein.*

$$C_{11}H_7N \atop CO-O \Big\rangle C \Big\langle {C_6H_3(NEt_2) \atop C_6H_3(NEt_2)} \Big\rangle O$$
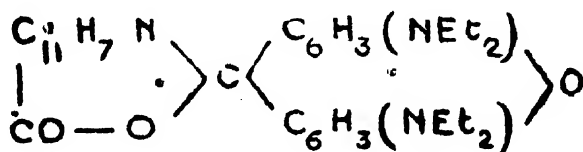
A mixture of β-phenyl-pyridine-dicarboxylic acid (1 mol.) and m-diethyl-amidophenol (2 mol.) was heated with a few drops of strong sulphuric acid at 160-170° for about two hours. The melt was then extracted with alcohol and the alcoholic extract, after filtration, was diluted with water which caused the precipitation of the

colouring matter in purple flocks. This was filtered and purified by dissolving in dilute hydrochloric acid and precipitating with dilute sodium carbonate. It is a reddish violet crystalline powder which dissolves in dilute acids and also in organic solvents, the solution has a brilliant pink colour and a brown fluorescence. It melts at 193°. (Found : $N = 9.07$. $C_{29}H_{23}O_3N_3$ requires $N = 9.1$ per cent.).

m-*Phenylene-diamine-β-phenyl-pyridine-dicarboxylein.*

$$C_{11}H_7N \Big\rangle_{CO-O} C \Big\langle \begin{matrix} C_6H_3(NH_2) \\ C_6H_3(NH_2) \end{matrix} \Big\rangle NH$$
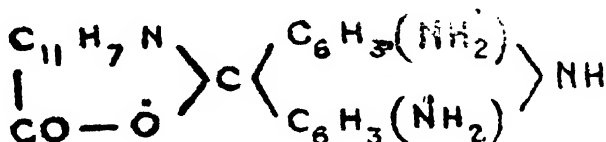
A mixture of β-phenyl-pyridine-dicarboxylic acid (1 mol.) and m-phenylene-diamine hydrochloride (2 mols. plus 10 per cent. excess) was heated at 180-190° for about three hours. The melt was allowed to cool and after grinding to a fine powder was extracted with absolute alcohol. The alcoholic extract after boiling with animal charcoal was concentrated to a small volume and the dyestuff crystallised as light brown needles. It melts with decomposition at 154° and dissolves, in organic solvents and dilute acids. The solution has an orange colour and a green fluorescence. (Found : $N = 13.5$. $C_{25}H_{19}O_2N_4$ requires $N = 13.7$ per cent.).

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Quinolino-bromopyrones and their Conversion into Quinolino-furans.

BY

BY

Biman Bihari Dey

BIMAN BIHARI DEY

AND

TIRUVENKATA RAJENDRA SESHADRI.

The bromination of quinoline-pyrones, dissolved in carbon tetrachloride or in glacial acetic acid, which was carried out with the intention of obtaining quinolino-bromopyrones, was found to proceed in a complex manner. On resorting to the bromo-nitro-, and the bromo-amino-coumarins (Dey and Row, *J. Chem. Soc.*, 1923, 113, 3 79) the authors found that quinolino-bromopyrones could be obtained from these through the Skraup and the Doebner-Miller synthesis. For instance :—
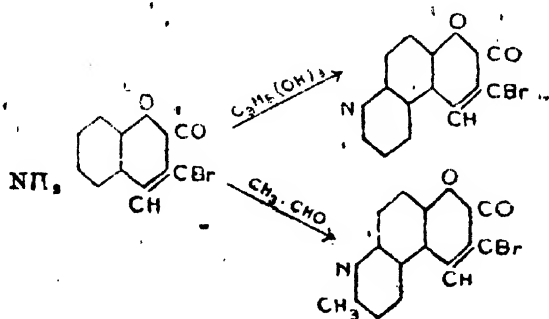
The quinolino-bromopyrones are colourless substances insoluble in water, dissolving very sparingly in alcohol, and more readily in boiling chloroform or in carbon tetrachloride which are the best media for crystallisation. The salts with hydrochloric, with nitric, and with sulphuric acid separate as crystals when a solution of the

base in the concentrated acid is diluted with about its own volume of water. The methiodides are partially resolved into their constituents on evaporating their aqueous solutions on the water-bath. The hydrogenations of the pyridine ring in these substances proceeds smoothly enough, the resulting tetrahydro-quinolino-bromopyrones resembling the reduction products of the unsubstituted quinolinopyrones in all respects, e.g., colour, crystalline form and solubility.

Cold dilute caustic soda has no appreciable action on these substances but on warming they gradually dissolve to an almost colourless solution from which acids of the coumaridic type are precipitated on acidification. The change, which is effected most readily by boiling alcoholic potash, is represented as follows :—
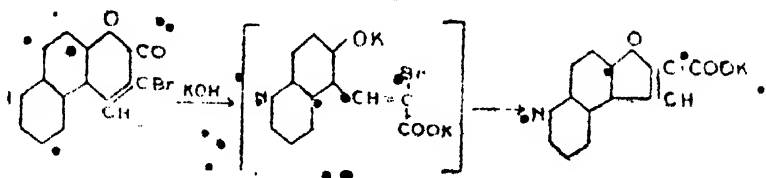
The quinolinofuran carboxylic acids obtained in this way crystallise from boiling water in soft, colourless needles, which are stable and neither melt nor decompose at temperatures below 300°. They have an amphoteric character, dissolving both in acids and alkalis in the cold and are esterified with case on saturating the alcoholic solution with hydrogen chloride, the ester hydrochlorides being deposited under these conditions. When warmed with sulphuric acid they display the change of colours characteristic of substances that have the benzo-furan structure. On heating with soda lime to dull redness, the acids split off carbon dioxide and yield the quinolino-furans, a class of heterocyclic substances that appears not to have been described before. These quinolino-furans

are pronounced bases, and readily dissolve in dilute acids from which ammonia precipitates them as white emulsions which slowly solidify on standing forming hard cubicals crystals. They are stable and remain unaffected by hot alkali.

EXPERIMENTAL.

Quinolino-6:5-a-3-bromopyrone.
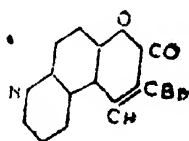
3-Bromo-6-nitro-coumarin (8 gms.) was intimately mixed with dry glycerol (10 c.c.), and sulphuric acid (8 c.c.) was slowly added with stirring. The mixture was heated gradually in an oil-bath; at about 140° a vigorous reaction took place and the mass began to swell. The flask was taken out of the oil-bath, shaken well and cooled, and when the vigour of the reaction had subsided, the temperature was slowly raised to 170° and kept between 170-180° for 6 hours. The dark mass was then cooled and extracted with boiling water repeatedly till the filtrate ceased to show any colour. The solution was rendered alkaline with soduim carbonate when a yellowish green flocculent precipitate of impure quinolino-bromo-pyrone separated.

It is insoluble in ether and in benzene and very sparingly soluble in cold alcohol: about 200 c.c. of boiling alcohol dissolve one gram. It dissolves very readily in chloroform or pyridine and crystallise from these solvents as colourless sharp needles, m.p. 236—237[b]. The pure product amounted to about 2 gms. (Found: Br = 29·2. $C_{12}H_6O_2NBr$ requires Br = 29·0 per cent.).

The *sulphate*, the *hydrochloride* and the *nitrate* were obtained as colourless needles when moderately concentrated solutions (4 *N*) of the respective acids were added to the solid substance; a clear solution was produced at first and very soon the salts began to crystallise.

The *oxalate* crystallised as long colourless fibres on adding a concentrated solution of oxalic acid to a solution of the base in dilute sulphuric acid.

The *picrate*, m. p. 255°, was deposited as stout yellow prisms when a saturated aqueous solution of picric acid was added to an acid solution of the substance.

The *dichromate* separated as four-sided prisms even from very dilute solutions.

The *ferrocyanide* formed thin plates of a pale yellow colour.

The *mercuri-chloride* separated from concentrated solutions as long, colourless needles, and the *mercuri-iodide*, which was amorphous at first, slowly changed into yellow pyramidal crystals.

The *chloroplatinate* formed pale yellow prismatic needles. (Found: Pt = 20·1 $(C_{12}H_9O_2NBr)_2$, H_2PtCl_6 requires Pt = 20·3 per cent.).

1:2:3:4-Tetrahydro-quinolino-6: 5-a-3-bromopyrone.

The above quinolino-bromopyrone (1 g.) was treated with (1:1 dilute) hydrochloric acid (40 c. c.) and granulated tin (4 g.) and the mixture was kept boiling gently for six hours. The clear solution was then diluted and the tin eliminated using sulphuretted hydrogen. The filtrate was then concentrated on the water-bath to small bulk and the tetrahydro compound was precipitated using dilute ammonia. It crystallises from alcohol in golden

yellow plates melting sharply at 174°; the pure substance weighed only 0·2 g. .(Found: Br = 28·65. $C_{12}H_{10}O_2NBr$ requires Br = 28·6 per cent.).

The *hydrochloride* crystallises as colourless needles from moderately concentrated solutions.

The *chloroplatinate* forms yellow sharp needles. (Found: Pt = 20·0. $(C_{12}H_{10}O_2NBr)_2$ H_2PtCl_6 requires Pt = 20·1 per cent.).

. The *nitroso compound* was thrown down as a flocculent precipitate when excess of dilute sodium nitrite solution was added to a solution of the tetrahydro compound in dilute hydrochloric acid. It was moderately soluble in boiling alcohol from which it crystallised as colourless rhombic plates, m. p. 195-196° (decomp.).

Quinolino-6:5-α-3-bromopyronemethiodide was prepared by heating the base with methyl iodide, with the addition of a little methyl alcohol, at 140° in a sealed tube for 3 hours. It dissolved in cold water to an almost colourless solution and crystallised, on concentrating the solution, as deep yellow rectangular plates, m. p. 252° (decomp.). On boiling the aqueous solution, the methiodide slowly decomposed, giving the original quinolino-bromopyrone.

Quinolino-6:5-furan-α-carboxylic Acid.
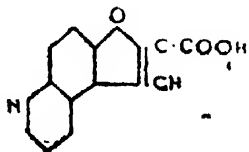
The quinolino-bromopyrone (2 g.) was dissolved in about 50 c.c. of alcohol, a strong solution of caustic potash (5 g. in 10 c.c. of water) was added, and the mixture was boiled under reflux for four hours. On

cooling, colourless crystals of the potassium salt of the furan carboxylic acid were deposited. Water was added until a clear solution was obtained and then carefully neutralised, when the acid was slowly deposited in the crystalline condition. It was fairly soluble in boiling water and boiling alcohol and crystallised from these solvents as colourless needles which neither melted nor decomposed below 300°. The yield was satisfactory, the pure product weighing 1·5 g.

The *silver* salt was obtained as a colourless, gelatinous precipitate. (Found : Ag = 33·4. $C_{12}H_6O_3NAg$ requires Ag = 33·8 per cent.).

The *ethyl ester* was prepared by saturating an alcoholic suspension of the acid with hydrogen chloride. The product was poured into water, neutralised with sodium bicarbonate and the precipitate crystallised from dilute alcohol. It was obtained as colourless felted needles m. p. 133°.

Quinolino-6 : 5-furan.
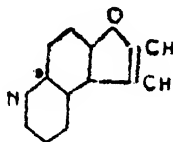
Quinolino-furan-carboxylic acid (2 g.) was intimately mixed with 5 times its weight of finely powdered dry sodalime and heated in a hard glass tube to dull redness for about an hour. An oil of a light brown colour having an odour somewhat resembling quinoline distilled which solidified as a hard crystalline mass. Recrystallisation from alcohol gave colourless plates m. p. 85°; the pure product weighed 0·6 g.

The substance is readily soluble in alcohol and in most of the ordinary organic solvents (ether, chloroform, benzene), the solutions exhibiting a pale blue fluorescence. It is insoluble in cold water and dissolves appreciably in boiling water, the clear solution becoming milky on cooling. (Found: $N = 8.5$. $C_{11}H_7NO$ requires $N = 8.3$ per cent.).

The quinolino-furan dissolved in cold dilute acid producing light green solutions from which it was re-precipited by the addition of ammonia. With concentrated sulphuric acid it gave a violet solution which changed to blue on warming.

The *picrate* formed light yellow prisms, m. p. $221°$.

The *dichromate* was obtained as red rhombohedral crystals, m. p. $149°$ (decomp.).

The *mercuri-chloride* crystallised as triangular plates when fairly concentrated solutions were employed and the *mercuri-iodide* separated as colourless needles when Meyer's reagent was added to a solution of the substance in dilute acids.

The *chloroplatinate* formed yellow needles. (Found: $Pt = 25.9$. $(C_{11}H_7NO)_2, H_2PtCl_6$ requires $Pt = 26.1$ per cent.).

Quinolino-6:5-furan Methiodide.—The solid furan was mixed with an excess of methyl iodide and a little alcohol and heated in a sealed tube at $100°$ for an hour. On cooling, the solution gave a mass of yellow four-sided prisms; the product, m. p. $284°$ (decomp.), was pure and the yield was almost theoretical.

The methiodide dissolved easily in cold water and warm alcohol producing pale green solutions which on concentration deposit the substance in a pure, crystalline condition. It is not perceptibly decomposed by boiling water. (Found: $I = 40.6$. $C_{11}H_7NO, CH_3I$ requires $I = 40.6$ per cent.).

3-Bromo-6-amino-coumarin.

3-Bromo-6-nitro-coumarin (2 g.) was treated with 4 *N*-acetic acid (100 c.c.), heated to about 100° on a boiling water-bath and fine iron powder (4 g.) was added in the course of an hour. The reaction product was cooled, made alkaline with sodium bicarbonate, the precipitate filtered and extracted with boiling alcohol. On cooling the amino compound crystallised as bright red needles, m. p. 192—193,° weighing 1·2 g. (Found: Br = 33·5. $C_9H_6O_2NBr$ requires Br = 33·3 per cent.).

2-Methyl-quinolino-6: 5-a-3-bromopyrone.
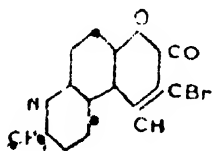
3-Bromo-6-amino-coumarin (2 g.) was treated with fuming hydrochloric and (10 c.c.) and paraldehyde (4 c.c.) added. After leaving over-night and then heating in an oil-bath for 2 hours at 130°, the resinous mass was extracted repeatedly with small quantities of boiling water till the filtrate ceased to be coloured. On rendering it alkaline with sodium carbonate, the methyl-quinolino-bromopyrone was obtained as a dark coloured flocculent precipitate; this was purified by redissolving in dilute hydrochloric acid and precipitating carefully with sodium carbonate.

It is sparingly soluble in alcohol, but readily dissolved in pyridine or chloroform and crystallised from these solvents as colourless rhombohedral crystals, m. p. 243° (decomp.). The pure product weighed a little less than

a gram. (Found: $Br = 27.6$. $C_{13}H_8O_2NBr$ requires $Br = 27.4$ per cent.).

The salts of methylquinolino-bromopyrone closely resembled those of quinolino-bromopyrone. ' The *hydrochloride*, *nitrate* and *sulphate* are sparingly soluble in water and crystallised from moderatly concentrated acid solutions as colourless needles, their aqueous solutions are colourless.

The *picrate*, light yellow prisms, m. p. 210°, the *dichromate*, deep yellow prisimatic needles, the *mercuri-chloride* colourless silky needles, the *mercuri-iodide*, yellow flat needles and the *ferrocyanide*, glistening yellow needless, were all prepared in the usual way from and solutions of the base.

The *chloroplatinate* crystallised in sheaves of yellow needles. (Found: $Pt = 19.7$. $(C_{13}H_8O_2NBr)_2$, H_2PtCl_6 requires $Pt = 19.7$ per cent.).

2-*Methyl*-1 : 2 : 3 : 4-*tetrahydro-quinolino*-6 : 5-a-3-*bromo-pyrone* was obtained in the usual way by reducing methyl-quinolino-bromopyrone 'with tin and hydrochloric acid. It crystallised from alcohol as rhombic plates, m. p. 162-163°. '(Found: $Br = 27.3$. $C_{13}H_{12}O_2NBr$ requires $Br = 27.3$ per cent.).

The *hydrechloride* ' of the base was precipitated from moderately concentrated solutions as colorless needles.

The *chloroplatinate* separated as yellow needles and the *nitroso compound* crystallised from alcohol as colourless needles, m. p. 179°.

2-*Methylquinolino*-6 : 5-a-3-*bromopyrone-methiodide*, obtained 'in the usual way,' crystallised from water in yellow plates, m. p. 285° (decomp.). It is insoluble in all the ordinary organic solvents and decomposed on prolonged boiling with water, regenerating the methyl-quinolino-bromopyrone.

2-Methyl-quinolino-6: 5-furan-a-carboxylic Acid.—This was obtained from 2-methyl-quinolino-6 : 5-a—bromo-pyrone by the action of alcoholic potash. It crystallised from boiling water or alcohol in colourless flat needles which do not melt below 300°. The yield was theoretical.

The *silver* salt was precipitated as a colourless flocculent precipitate. (Found: Ag = 32·1. $C_{13}H_8O_3NAg$ requires Ag = 32·3 per cent.).

The *ethyl ester* when crystallised from dilute alcohol appeared as clusters of colourless needles, m. p. 107°.

2-Methyl-quinolino-6:5-furan.—This was obtained from 2-methyl-quinolino-furan-carboxylic acid by distillation with dry sodalime. It distilled as a light brown oil which when cooled in ice immediately and scratched became a crystalline solid melting at 29° approximately. On allowing the oil to stand for 24 hours, however, it solidified as a mass of colourless cubes, m. p. 84-85°: 0·6 g. of the furan was obtained by distilling 2 g. of the acid.

The methyl-quinolino-furan is readily soluble in the ordinary organic solvents, the solutions exhibiting a pale blue fluorescence. Though it is not perceptibly soluble in cold water, it dissolved to a considerable extent in boiling water. With concentrated sulphuric acid it gave a violet solution which changes to blue on warming. (Found: N = 7·8. $C_{12}H_9NO$ requires N = 7·7 per cent.).

The *hydrochloride*, *sulphate* and the *nitrate* are all readily soluble in water, the aqueous solutions exhibiting a faint green colour. The *picrate* crystallised as yellow prisms, m. p. 198°; the *dichromate* forms red needles, m. p. 152° (decomp.); the *ferrocyanide* is slowly deposited as light yellow plates from concentrated solutions, and the *mercuri-chloride* and the *mercuri-iodide* form clusters of colourless and light yellow needles respectively.

15

The *chloroptatinate* sepatrated as tufts of yellow needles. (Found : Pt = 25·0. $(C_{12} H_9 NO)_2$, H_2PtCl_6 requires Pt = 25·1 per cent.).

2-*Methyl-quinolino*-6:5-*furan-methiodide*, obtained in good yield, crystallised from dilute alcohol in bright yellow needles, m. p. 256° (decomp.). Its solutions in water and alcohol have a light green colour. (Found : I = 39·2. $C_{12}H_9NO$, CH_3I requires I = 39·1 per cent.).

Influence of the Hydrolysis of Gelatine on Gold Numbers and Peptisation of other Substances.

BY

PHANI BHUSAN GANGULY.

The impurities generally found in commercial gelatine fall under two heads, ionogenic matter and non-ionogenic matter, the latter mostly produced by the partial decomposition of the gelatine. The ionogenic matter generally present are the calcium salts. of phosphoric acids, the non-ionogenic matter being mostly gelatoses, intermediate hydrolysis products of gelatine. The presence of, these, impurities changes the properties of gelatine in a remarkable way. It was shown by Liesegang (*Zeit. physikal. Chem.*, 1914, 88, 1) that gelatine free from these impurities is incapable of producing Liesegang structures, a certain amount of gelatose and acid being necessary. It has been found that although a small amount of gelatose can render gelatine capable of producing banded structures, the addition of acids alone cannot produce that effect. In view of the above it seemed desirable to investigate the influence of the impurities generally found in gelatine on the peptising properties of gelatine.

The gelatine was purified by washing till the ash content was below 0·1 per cent. This purified gelatine can be kept for days without developing any signs of decay. It is nevertheless undergoing a decomposition which changes its p_H value in a marked way. Hence in the following experiments immediately before use the

gelatine was washed twice with distilled water, the water being in contact with the gelatine each time for about half an hour.

To find the strength of the gelatine solutions used in these experiments, a measured volume was evaporated to dryness in an air chamber maintained at a temperature of 90-100°. Dry gelatine cannot be weighed in the ordinary way as it takes up moisture too quickly. A tube with a bulb blown at one end with a side tube furnished with a tap was used. The bulb was blown fairly thick so as to be strong enough to be able to stand the pull of the drying gelatine. After the gelatine solution had dried the tube was closed while hot and allowed to cool down to the temperature of the room. Dry air was then allowed to leak in with the help of the tap. Even small quantities of gelatine could be weighed quite consistently by this method.

A solution of colloidal gold was prepared by Zsigmondy's method, and the gold numbers of commercial and purified gelatine were determined. In every case in these experiments the final solution was prepared by diluting in the same way. In a preliminary experiment the gold numbers of purified and commercial gelatine were as follows :—

	1st set.	2nd set.
Pure gelatine ...	0·014	0·016
Commercial gelatine ...	0·022	0·028

The values for the commercial gelatine showed great fluctuation and were much higher than the values for the corresponding purified gelatine. As the commercial gelatine contained the various ionogenic impurities as well as the degradation products of gelatine no information can be obtained from the foregoing results. Hence it was decided to change the factors one at a time.

A freshly prepared sample of gelatine was taken and a solution prepared. The solution was estimated, the necessary dilution made, and the gold number determined. To determine the gold number 10 c.c. of the gold sol were thoroughly mixed with the added amount of gelatine and kept aside for about 15 minutes before the addition of the 1 c.c. of the 10 per cent. sodium chloride. The values of the gold number have all been expressed in terms of anhydrous gelatine. A portion of the same gelatine was kept apart moist for about two nights so as to undergo partial hydrolytic and other decompositions. The gold numbers of this gelatine were then determined and the following values obtained :—

Freshly purified gelatine.

Vol. gelatine added. (0·00125 %)	Colour.	Gold number.
1·0 c.c.	Blue.	
1·2 c.c.	Purple.	
1·3 c.c.	Purplish red.	0·016.
1·4 c.c.	Red.	

Same gelatine kept moist for two days.

Vol. gelatine added. (0·00125 %)	Colour.	Gold number.
0·6 c.c.	Blue	
0·7 c.c.	Bluish purple.	
0·8 c.c.	Purple.	0·01.
1·0 c.c.	No change.	

There is thus a marked difference in the values of the gold numbers which clearly shows that gelatine when

left moist for some time undergoes a change which renders it a better peptising agent.

To investigate the above point further the influence of the decomposition of gelatine brought about by free boiling of a solution of gelatine on gold numbers was investigated. A one per cent. solution of commercial gelatine was taken and boiled freely in a silica vessel, care being taken to prevent the gelatine drying on the walls of the vessel. At the end of every two hours the solution was cooled to the temperature of the room and the volume of the liquid brought back to its original value. A solution was prepared by diluting the calculated volume and the gold number determined. The results are given in the following table :—

	Time (hours).	Gold numbers.
1.	0	0·020
2.	2	0·020
3.	4	0·018
4.	6	0·014
5.	8	0·012
6.	10	0·010
7.	12	0·012
8.	14	0·018
9.	18	0·026
10.	20	0·034

From the above we see that when gelatine is freely boiled we get in the beginning an increase in the peptising properties of gelatine which, however, after a time, begins to fall and attains a value much below the initial value.

When gelatine is freely boiled it undergoes a change. A part of it is hydrolised, producing gelatoses and other intermediate hydrolytic products of gelatine. Evidently the presence of these earlier hydrolytic products of gelatine increases its peptising value as is clearly seen from the marked fall in gold numbers. On further boiling more and more of the final products of hydrolysis of gelatine are produced at the expense of the original gelatine and hence there is a rise in gold numbers.

Another possible influence of boiling is the change in size of the particles of gelatine. In the beginning boiling disintegrates any gel aggregation that might have been formed thus producing gelatine solutions containing particles of a uniform and probably smaller size. As however the above gelatine solutions were prepared in identical conditions this influence, if any, will be very small.

The question of the size of gelatine particles on its peptising properties has been thoroughly investigated by Menz (Zeit. physikal. Chem., 1909, 66, 129). He found that the gold number decreases remarkably as the original gelatine solution from which the final dilute solution is prepared gets more and more dilute. The change is due to the presence at the lower dilutions of a larger number of finer particles which are more efficient than, larger particles in peptising gold sols. Menz's dilute solutions were all prepared at the room temperature. In the following experiments in order to investigate the influence of temperature on the size of the particles all the dilute solutions have been prepared at 70°.

One gram of gelatine was allowed to swell in contact with water for several hours. It was then warmed up to 70° and the volume made up very nearly up to 100 c.c. at 70°. The solution was then cooled to the room temperature and the volume accurately made up. The

same procedure was adopted to get further dilutions, the final solution being 0·001 per cent. solution. The results obtained are given in the following table :—

Original gelatine solution.	Vol. gelatine added.	Colour.	Vol. gelatine added.	Colour.
1 per cent.	1·2 c.c.	Purple	1·0 c.c.	Purple (bluish)
0·5 ,,	1·2 c.c.	Purplish red	1·0 c.c.	Purple (bluish)
0·1 ,,	1·2 c.c.	Red purplish	1·0 c.c.	Purple
0·01 ,,	1·2 c.c.	Red	1·0 c.c.	Purple
0·001 ,,	1·2 c.c.	No change.	1·0 c.c.	Purple

So far as it could be distinguished by observing the colour changes practically no decrease in the gold number with the dilution of the original gelatine solutions was observed when the dilution was done at 70°. From the above it seems reasonable to deduce that up to a concentration of 1 per cent. the particles in a gelatine solution are practically of the same size at a temperature considerably above the gelation temperature of gelatine.

Elliott and Sheppard (*J. Ind. Eng. Chem.*, 1921, *13*, 699) have, however, obtained remarkable differences in gold numbers even when the dilution was done at a temperature of 50°, which is not borne out by the above experiments. It is well known that a one per cent. gelatine solution when kept at room temperature for several hours will set into a gel. When this is shaken up with water the gel is torn into smaller fragments. If shaken for a sufficiently long time a solution is obtained which contains particles of all different sizes from about molecular dimensions to the size of about 9μ. Menz showed by ultramicroscopic examinations that such a solution contained particles of the size $2—9\mu$. The presence of coarser particles can easily be seen from the

fact that even after two hours of vigorous shaking the resulting solution contained particles big enough to be separated by an ordinary filter paper. These particles which are stopped by the filter paper may very appropriately be looked upon as fragments of the original gel which have not gone into solution. This is tantamount to saying that the final gelatine solution is actually weaker than what it is supposed to be. Consequently a higher gold number will be expected irrespective of the influence of the size of gelatine particles on its peptising properties. This should be taken into consideration when drawing any conclusions from the rise in gold numbers as obtained by Menz and repeated by others. On the other hand when the gel is warmed to a temperature of 70° and then diluted the total quantity of gelatine goes into solution and hence practically the same gold number is obtained irrespective of the process of dilution.

The influence of the quality of gelatine on the peptising power of gelatine in cases of precipitates has been studied in the cases of silver and lead chromates. These substances were formed by mixing dilute solutions of the respective nitrates with the exact chemically equivalent amounts of potassium chromate. From preliminary experiments the quantity of gelatine was so adjusted that by using different volumes of the reacting substances, peptised solutions of different degrees of turbidities were obtained. To compare the turbidities of the different mixtures a simple arrangement was set up as shown in the diagram. The light is divided into two beams by means of the screen, S containing two semi-circular apertures p_1 and p_2. One beam of light passes through the liquid under examination contained in the cell C, whilst the other beam reaches the reflecting surface R after passing through a piece of milk glass m. Liquid is run into the cell C till the intensity of both the spots of
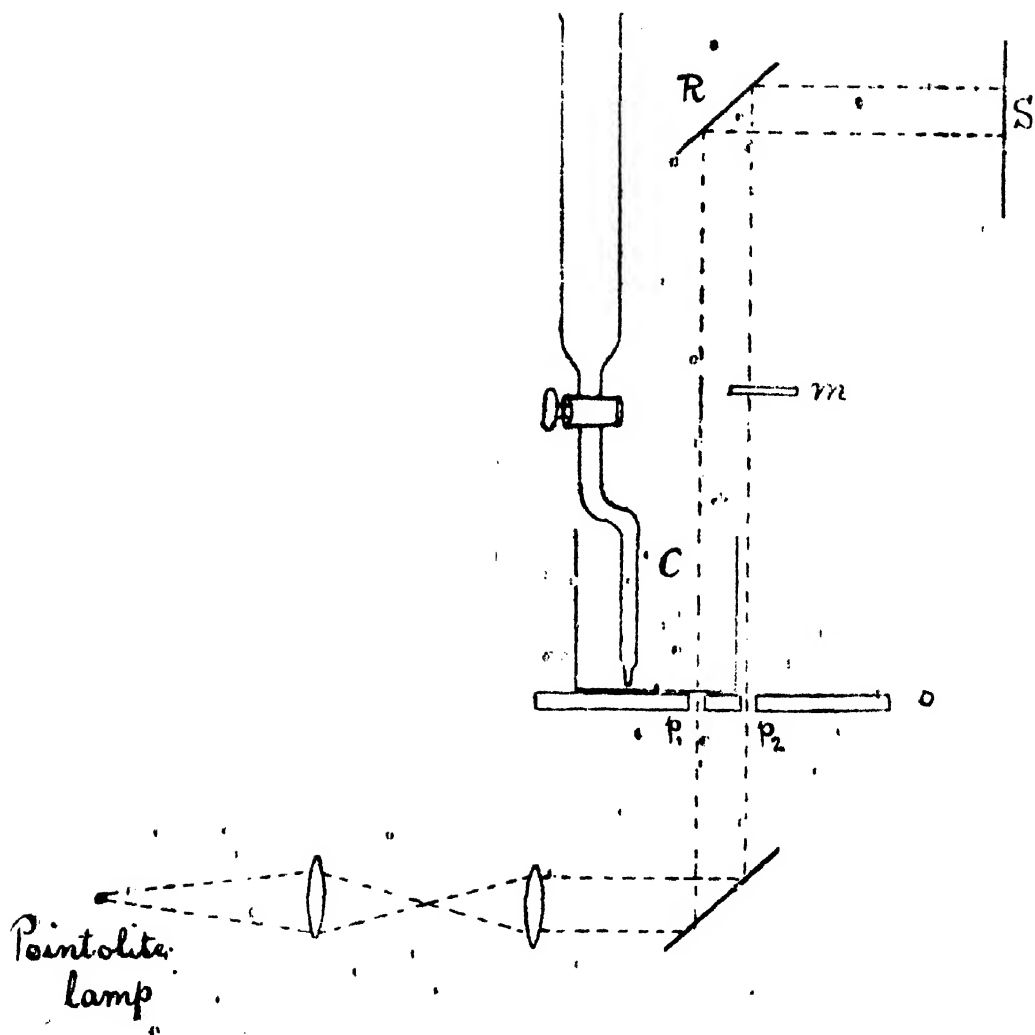
light on the screen *S*, which is protected from all extraneous light, is about the same. Two series of experiments were performed using fresh gelatine in one case, and the same amount of partially hydrolysed gelatine in the other case. 0·4 c.c. of a one per cent. gelatine solution were added to different volumes of the reacting substances, the total volume in each case being brought up to the same value. The results are given in the following table:—

	AgNO$_3$ 3·502 per cent.	K$_2$CrO$_4$ 2·0 per cent.	Turbidity readings.	
			Pure gelatine	Hydrolysed gelatine
1.	0·2 c.c.	0·2 c.c.	Completely precipitated.	Partially precipitated.
2.	0·3 c.c.	0·3 c.c.	Precipitated in 24 hours.	Stable sol.
3.	0·4 c.c.	0·4 c.c.	5·5 c.c.	11·3 c.c.
4.	0·5 c.c.	0·5 c.c.	6·0 c.c.	10·0 c.c.
5.	1·0 c.c.	1·0 c.c.	4·5 c.c.	7·0 c.c.
6.	1·5 c.c.	1·5 c.c.	Precipitated on standing.	Partially precipitated.
7.	2·0 c.c.	2·0 c.c.	Immediately precipitated.	Immediately precipitated.

From the above it will be seen that partially hydrolysed gelatine is more efficient in peptising silver chromate than pure gelatine. Similar results were obtained with lead chromate.

It will be interesting to recall that Zunz (*Arch. Internat. Physiol.*, 1904, 1, 127) has obtained similar marked differences in the peptising properties of

albumoses, the decomposition products of egg albumin. The synalbumoses have no protective action on gold, whilst the proalbumoses have a fairly good peptising power (*cf.* Zsigmondy, *Chemistry of Colloids*, p. 108). It thus seems to be a general property shown by protein and similar bodies of being a better peptising substance when partially hydrolysed.

Summary.

1. Solutions of gelatine containing a certain amount of gelatose and other earlier hydrolysis products of gelatine have been found to be more efficient in peptising gold sols than solutions of purified gelatine.

2. Dilute gelatine solutions prepared from a one per cent. gelatine gel at 70° gave practically the same gold numbers and thus failed to show the effects observed by Elliott and Sheppard at 50°.

3. Partially hydrolysed gelatine is a better peptising agent for silver and lead chromates than pure gelatine.

Quinolino-6 : 5-α-pyrones

By

Biman Bihari Dey, Indubhusan Sarkar and
Tiruvenkata Rajendra Seshadri.

It has been shown (Dey and Goswami, *J. Chem. Soc.*,
1919, 115, 531) that a class of heterocyclic substances
containing the pyridine, benzene and pyrone-rings fused to
one another in the order named could be synthesised by
the application of the Skraup reaction to aminocoumarins.
These compounds were termed the ψ-1 :· 8-*iso*napath-
oxazones, but in view of the publication of a paper on the
same subject under the title of "coumaro-quinolines"
(Kondo and· Tetsukichi Ui, *J. Pharm. S c., Japan,* 1923,
498, 615), it is now proposed to redesignate these substan-
ces the quinolino-α-pyrones, a name which offers a better
guide to the constitution of these substances than what
was suggested before.

The different positions in these heterocyclic ring-systems may be conveniently numbered as follows :
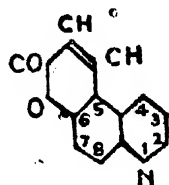
Quinolino-6 : 5-
a-pyrone
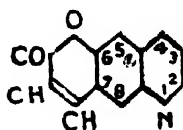
Quinolino-6 : 7-
a-pyrone.
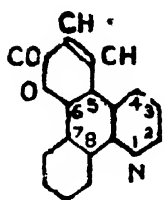
7 : 8-Benzo-
quinolino-
6 : 5-a-pyrone
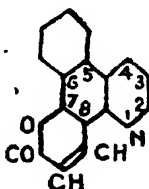
5 : 6-Benzo-
quinolino-
7 : 8-a-pyrone
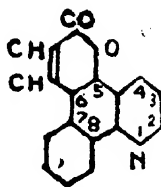
7 : 8-Benzo-
quinolino-
5 : 6-a-pyrone

In view of the interest attaching to these substances and the possibility of their exhibiting physiological activity, it seemed desirable to extend the series by studying methods of synthesis other than the Skraup process. An account is now given of the results of applying the Doebner-Miller reaction to 6-amino-coumarin, and to 6-amino-4-methyl-a-naphthapyrone. The former substance, reacting with paraldehyde, and with a mixture of paraldehyde and acetone, gave 2-methyl- and 2 : 4-dimethyl-quinolino-6 : 5-a-pyrone respectively, presumably in accordance with the following scheme :—

$$CH_3.CHO + CH_2.COX = CH_3.CH(OH) CH_2COX$$

6-Amino-
coumarin

$+ H_2O + H_2$
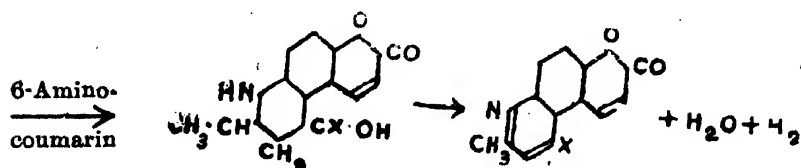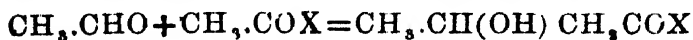
where X is H or CH_3.

The assumption that the amino-group reacts in the first

place with the hydroxy-group of the aldol molecule seems to afford the simplest explanation of the mechanism of this change and is also supported by the observation that in the parallel reaction, between crotonic aldehyde and aniline, α-methyl-quinoline is almost exclusively formed.

The 2-methyl-quinolino-pyrone was obtained quite readily in a pure state, but in the preparation of the 2 : 4-dimethyl derivative the mixture of aldehyde and acetone had to be kept, saturated with hydrochloric acid, for about forty-eight hours before adding the amine hydrochloride: as on omitting this precaution considerable quantities of the monomethyl derivative were simultaneously formed and the separation of the mixture was found to be difficult and tedious.

These methyl derivatives do not differ materially in their general properties from the unsubstituted quinolino-pyrones described before. Their methiodides, however, are formed less readily and are also unstable, being partly decomposed into their constituents by boiling water. These methiodides have a pronounced yellow colour, but are colourless in aqueous solutions (cf. Dey and Goswami, loc. cit., 534).

Reduction of the methyl-quinolino-pyrones with tin and hydrochloric acid led to hydrogenation of the pyridine ring, but the process was slow and, in the case of the 2 : 4-dimethyl compound, the yield of the tetrahydro-derivative did not exceed 10 per cent. of the theoretical. This result is in agreement with the observation made by Braun, Gmelin and Schultheiss (Ber., 1923, 56, 1338), viz., that substitution of the pyridine ring by alkyl groups renders it more resistant to reduction. 2-Methyl-quinolino-6 : 5-α-pyrone, forms a benzylidene derivative. This is colourless, but its hydrochloride and sulphate, which are sparingly soluble in water, have a bright yellow colour.

EXPERIMENTAL.

2-Methyl-quinolino-6 : 5-a-pyrone.
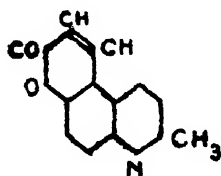
A mixture of 6-amino-coumarin (4 g.), fuming hydrochloric acid (10 c.c.), and paraldehyde (8 c.c.) was cooled in ice, saturated with hydrogen chloride and left overnight at the laboratory temperature in a loosely corked flask. The dark viscous product was heated at 130-135° for 3 hours, and the nearly dry mass was crushed and extracted with small quantities of boiling water until the solution was colourless. The extracts were cooled, and made alkaline with solid sodium bicarbonate, the yellow flocculent precipitate obtained in this way crystallised from 50 per cent. alcohol in pale yellow needles, m. p. 212 – 214° (yield 2 – 2·4 g.). The substance, on being twice crystallised from rectified spirit with the aid of animal charcoal, gave long colourless needles, m. p. 219 – 220°. (Found.: C = 73·8 ; H = 4·3 ; N = 6·3. $C_{13}H_9O_2N$ requires C = 73·9 ; H = 4·3 ; N = 6·6 per cent.)

The substance is insoluble in cold water, very sparingly soluble in ether, benzene, petroleum, or cold 90 per cent. alcohol, moderately soluble in boiling water, and easily soluble in hot alcohol, chloroform and pyridine. When freshly precipitated, it dissolves in cold 10 per cent. caustic soda solution, but is insoluble in aqueous sodium carbonate or ammonia. 2-Methyl-quinolino-6 : 5-a-pyrone, is soluble in hydrochloric, nitric or sulphuric acid (equal vols. of the concentrated acid and water), but from the clear solutions the respective salts

soon separate in colourless needles. (Found : Cl=14·6. $C_{13}H_9O_2N$, HCl requires Cl=14·3 per cent.)

The *mercurichloride* was obtained, as a mass of soft colourless needles, and the *mercuri-iodide* as a pale yellow amorphous precipitate which slowly changed on standing to rhombic plates.

The *dichromate* crystallised from hot water in prismatic needles, deep yellow in colour. (Found : Cr_2O_3= 21·6. $(C_{13}H_9O_2N)_2$, $H_2Cr_2O_7$, $3\frac{1}{2}H_2O$ requires Cr_2O_3= 21·6 per cent.) The water of crystallisation in the dichromate could not be estimated as it was converted into a dark resinous mass at 100°.

The *picrate* crystallised from dilute alcohol in bright yellow needles. (Found : N=12·3. $C_{13}H_9O_2N$, $C_6H_3O_7N_3$ requires N=12·7 per cent.)

The *chloroplatinate* crystallised in yellow plates from hot water in which it dissolved very sparingly. (Found : Pt=23·5. $(C_{13}H_9O_2N)_2$, H_2PtCl_6 requires Pt=24·0 per cent.).

The *methiodide* was prepared by heating the base (1·5 g.), methyliodide (1 c.c.) and methyl alcohol (5 c.c.) in a sealed tube at 100° for five hours. The product was extracted thrice with hot water, and the combined extracts were cooled, filtered from unchanged base, and evaporated in a vacuum over sulphuric acid, when golden yellow rectangular plates of the methiodide separated ; m. p. 244-245° (decomp.). (Found : I=36·1. $C_{14}H_{12}O_2NI$ requires I=36·0 per cent.)

The methiodide dissolves readily in cold water, is insoluble in ether or benzene, and is decomposed by hot absolute alcohol.

The *benzylidene* derivative was prepared by heating the base (2 g.) with benzaldehyde (2 g.) at 150-160° and

adding freshly fused zinc chloride (3 g.) from time to time.' The dark viscous product which solidified on cooling, dissolved almost completely in boiling $2N$-hydrochloric acid. The *hydrochloride*, which separated in bright yellow needles almost completely on cooling, was collected. (Found: $Cl = 10\cdot7$. $C_{20}H_{13}O_2N$, HCl requires $Cl = 10\cdot6$ per cent.) The hydrochloride was decomposed with cold dilute ammonia and the *benzylidene* compound was crystallised from absolute alcohol which deposited colourless stout needles, m. p. 205°. (Found: $N = 4\cdot8$. $C_{20}H_{13}O_2N$ requires $N = 4\cdot7$ per cent.)

2-*Methyl*-1 : 2 : 3 : 4-*tetrahydroquinolino*-6 : 5-*a-pyrone*.

A solution of the quinolino-pyrone (2 g.) in 40 c.c. of dilute hydrochloric acid (1 : 1) was gently boiled for 5 hours with granulated tin (6 g.) ; the solution was diluted to 200 c.c., filtered, and the dissolved tin removed as sulphide. The filtrate was concentrated on the water-bath to about 100 c. c., cooled, and neutralised with ammonia, when the *tetrahydro-dreivative* slowly crystallised in small glistening plates of a golden yellow colour. Crystallised once from 50 per cent. alcohol, it melted sharply at 179° (yield 1-1·2 g.). (Found: $N = 6\cdot4$. $C_{13}H_{13}O_2N$ requires $N = 6\cdot5$ per cent.).

The *hydrochloride* crystallised from strong solutions in long colourless needles.

On treatment with nitric acid, the tetrahydro-compound developed a deep pink colour. A similar result was produced in an attempt to prepare the dichromate when the substance darkened and gradually decomposed.

The *picrate* and the *chloroplatinate* formed clusters of sharp pale yellow needles. (Found: $Pt = 23\cdot00$. $C_{13}H_{13}O_2N$, H_2PtCl_6 requires $Pt = 23\cdot2$ per cent.)

The N-*nitroso*-derivative, prepared in the usual manner, crystallised from alcohol in colourless prismatic needles, m. p. 160-161°. (Found: $N = 11 \cdot 0$. $C_{13}H_{12}O_3N_2$ requires $N = 11 \cdot 4$ per cent.).

The *acetyl* derivative separated from alcohol in colourless plates, m. p. 138-139°, and the *methiodide* from concentrated aqueous solutions in yellow plates, m. p. 202° (decomp.). (Found: $I = 35 \cdot 7$. $C_{14}H_{16}O_2NI$ requires $I = 35 \cdot 6$ per cent.).

2-Methyl-7:8-benzoquinolino-6:5-a-4'-methyl pyrone.
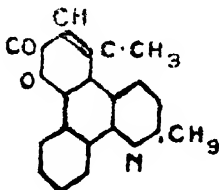
A mixture of 6-amino-4-methyl-1:2-naphthapyrone (2 g.), fuming hydrochloric acid (5 c.c.), and paraldehyde (6 g.) was saturated with hydrogen chloride and the product worked up as before. The product was yellow owing to the presence of some unchanged amino-naphthapyrone: it was therefore acetylated and the quinolino-pyrone extracted with cold dilute hydrochloric acid. Alkali precipitated from the extract a colourless solid which was insoluble in water, sparingly soluble in alcohol, and more readily soluble in chloroform or pyridine. It was best crystallised from chloroform which gave colourless prismatic needles, m. p. 248° (yield 0·6 gm.). (Found: $C = 78 \cdot 35$; $H = 4 \cdot 75$. $C_{19}H_{13}O_2N$ requires $C = 78 \cdot 5$; $H = 4 \cdot 7$ per cent.).

The *hydrochloride* separated from a concentrated solution in small, colourless needles, and the *picrate*, from alcohol, in yellow prisms.

3

The *dichromate* formed dark yellow, short, prismatic needles. (Found: $Cr_2O_3 = 20\cdot0$. $(C_{18}H_{13}O_2N)_2$, $H_2Cr_2O_7$ requires $Cr_2O_3 = 19\cdot8$ per cent.)

The *chloroplatinate* crystallised in pale yellow, rhombic plates. (Found: $Pt = 20\cdot5$. $(C_{18}H_{13}O_2N)_2$, H_2PtCl_6 requires $Pt = 20\cdot3$ per cent.)

The *mercurichloride* separated from concentrated solutions in lustrous triangular plates, and the *mercuri-iodide* formed pale yellow, prismatic needles.

2-*Methyl*-1 : 2 : 3 : 4-*tetrahydro*-7 : 8-*benzoquinolino*-6:5-*a*-4'-*methylpyrone*

This was prepared by reducing the naphthaquinolino-pyrone with tin and hydrochloric acid and working up the product as before. It crystallised from alcohol in yellow needles, m. p. 204°. (Found: $C = 77\cdot65$; $H = 6\cdot2$. $C_{18}H_{17}O_2N$ requires $C = 77\cdot8$; $H = 6\cdot0$ per cent.).

The *chloroplatinate* formed pale yellow tapering needles. (Found: $Pt = 20\cdot1$. $(C_{18}H_{17}O_2N)_2$, H_2PtCl_6 requires $Pt = 20\cdot1$ per cent.)

The N-*nitroso*-derivative crystallised from alcohol in colourless needles, m. p. 168° (decomp.), and the *acetyl* derivative formed colourless plates, m. p. 202°.

2 : 4-*Dimethyl-quinolino*-6 : 5-*a*-*pyrone*.
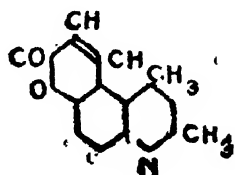
A mixture of paraldehyde and acetone (1 : 1) was kept saturated with hydrogen chloride for 2 days. To

10 c.c. of it a mixture of 6-aminocoumarin (4 g.) and fuming hydrochloric acid (10 c.c.) was added and the whole was saturated with hydrogen chloride and left at the ordinary temperature for 24 hours. The reaction was then completed by heating at 130-140° for 4 hours and the dry mass was worked up as before. The product still contained a small quantity of the α-methyl derivative which was removed by washing twice with a little boiling alcohol in which the dimethyl compound dissolved rather sparingly. It was finally crystallised from hot pyridine and a little water, separating in colourless needles, m. p. 265°. The amount of the pure product obtained seldom exceeded 1·5 gm. (Found: C=74·5; H=5·4; N=6·0. $C_{14}H_{11}O_2N$ requires C=74·7; H=4·9; N=6·2 per cent.)

The *hydrochloride* formed colourless cubical crystals. (Found: Cl=13·75. $C_{14}H_{11}O_2N$. HCl requires Cl=13·6 per cent.).

The *dichromate* crystallised in deep yellow needles.

(Found: Cr_2O_3=23·15. $(C_{14}H_{11}O_2N)_2$, $H_2Cr_2O_7$ requires Cr_2O_3=22·75 per cent.)

The *chloroplatinate* formed yellow plates. (Found: Pt=22·7. $(C_{14}H_{11}O_2N)_2$, H_2PtCl_6 requires Pt=22·7 per cent.)

The *picrate* crystallised from alcohol in short, stout, pale yellow needles. (Found: N=11·7. $C_{20}H_{14}O_9N_4$ requires N=12·3 per cent.)

The *mercurichloride* formed colourless prisms.

2 : 4-*Dimethyl*-1: 2 : 3 : 4-*tetrahydro-quinolino*-
6 : 5-*a-pyrone*.

After reduction with tin and hydrochloric acid for more than 12-hours, 2 g. of the dimethyl compound gave only 0·2 g. of the tetrahydro derivative crystallising from dilute alcohol in golden yellow rectangular plates, m. p. 121°. The unchanged material was mostly recovered being practically insoluble in dilute alcohol. (Found: $N = 6·3$. $C_{14}H_{15}O_2N$ requires $N = 6·1$ per cent.)

The N-*nitroso* derivative formed clusters of colourless needles melting at 177°, and the *benzoyl* derivative crystallised from glacial acetic acid in colourless, elongated plates, m. p. 171°.

Thiodiazines.

Part IV.

BY

PRAFULLA KUMAR BOSE.

Derivatives of thiol-thiodiazine are readily obtained by the condensation of benzyl- and nitrobenzyl-dithio-carbazinates with a halogenated esters in presence of a suitable condensing agent (Bose, this *Journal*, 1926, *3*, 148).

The investigation of thiodiazines has now been continued by studying the condensation of esters of phenyldithiocarbazinic acid with ω-bromoacetophenone and with p-methyl-ω-bromoacetophenone. This leads to the production of substances that show *cis-* and *trans-* isomerism and that can be converted into thiol-thiodia-zines.

In alcoholic solution alkyl-phenyl-dithiocarbazinates and ω-bromoacetophenone reacted so as to give rise to uncrystallisable oils, the formation of which was traced to the influence of hydrobromic acid liberated in the reaction. For, if the hydrobromic acid is neutralised as soon as it is formed or if the condensation proceeds in presence of the calculated amount of alkali, crystalline products of condensation, having the composition $Ph \cdot NH \cdot N : C(SAlk) \cdot S \cdot CH_2 \cdot CO \cdot Ph$, are obtained in good yield. The course of the reaction, however, was found to be greatly influenced by the method of neutralising hydrobromic acid. Thus when an alcoholic solution of a mixture of methyl-phenyldithiocarbazinate and

ω-bromoacetophenone was treated with the calculated quantity of alcoholic potash at the ordinary temperature, a bright yellow crystalline product, m. p. 100°, was obtained. If, however, an alcoholic solution of ω-bromoacetophenone is added to a mixture of equimolecular quantities of the ester and alcoholic potash, the condensation product consists of pale yellow soft needles, m. p. 93°. The two products are isomeric. Such isomerides have also been obtained with ethyl- and *n*-propyl-phenyldithiocarbazinates on the one hand and, ω-bromoacetophenone and *p*-methyl-ω-bromoacetophenone on the other.

The compounds, obtained by the first method, are brittle, deep yellow crystalline substances having, as a rule, higher melting points than the corresponding isomerides. They are further characterised by their sparing solubility in ligroin, by their capacity to yield phenylhydrazones, and their stability.

The isomeric compounds, obtained by the other method, are soft pale yellow crystalline substances, which are extremely soluble in most organic media and are even easily soluble in ligroin. Moreover, they fail to yield phenylhydrazones under the conditions employed for their isomerides and are unstable.

Hantzsch and Werner's theory of the spatial arrangement of atoms or groups about the system $>C=N-$ has been applied to the mono- and the di-alkyl-phenyldithiocarbazinates. It was found that aldehydes condense with the mono-alkyl compound to give thiodiazoles, thus:

$$R'CHO + \begin{matrix} Ph.NH.N \\ \| \\ HS.C.SR \end{matrix} = R'CH < \begin{matrix} Ph-N-N \\ \| \\ S-C.SR \end{matrix} + H_2O$$
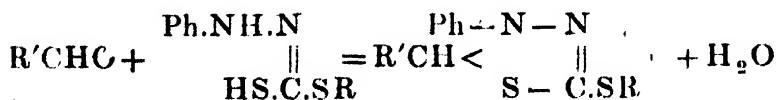
These mono-alkyl compounds were, therefore, regarded as having the thiol group in the *cis*-position relative to the anilino group (*cis*-thiol configuration).

From these mono-alkyl compounds, by the action of alkyl iodide, Busch was able to obtain dialkyl-phenyl-dithiocarbazinates of the type $PhNH \cdot N : C(SR)(SR')$.

$$PhNH \cdot N \atop \underset{HS.C.SR}{\|} \quad \text{and } R'I \text{ gave chiefly} \quad PhNH.N \atop \underset{R'S.C.SR}{\|}$$

$$Ph.NH.N \atop \underset{HS \cdot C \cdot SR'}{\|} \quad \text{and } RI \text{ gave chiefly} \quad Ph.NH.N \atop \underset{RS \cdot C \cdot SR'}{\|}$$
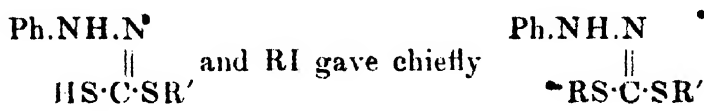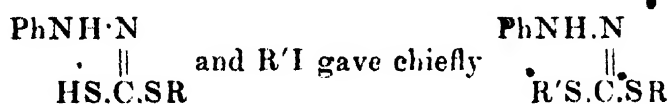
(Busch, *Ber.*, 1901, *34*, 1119; Busch and Kraft, *J. pr. Chem.*, 1911, [ii] *84*, 293.) Thus there are two iso-merides of the type $PhNH \cdot N = C(SR)(SR')$: the second alkyl group that is introduced occupies the *cis*-position with respect to the anilino group.

But it has already been stated that the isomerides of phenacyl and of *p*-methylphenacyl-alkyl-phenyldithio-carbazinate can be obtained from the same components under different conditions of experiment. Evidently the suggestion of Busch (*loc. cit.*) that mono-alkyl-phenyl-dithiocarbazinates react in the *cis*-thiol form only cannot be maintained in its entirety. The present author has, however, reasons to believe that the con-figurations given by Busch to his alkyl derivatives of phenyldithiocarbazinic acid are correct. On this analogy the pale yellow compounds, referred to above, would receive the formula (II). Consequently the bright yellow isomerides of higher melting point would be represented by (I), that is, by *trans*-configuration.

$$Ph.NH.N \atop \underset{RS.C.S.CH_2CO.Ph(p\text{-Tol-})}{\|} \qquad\qquad Ph.NH.N \atop \underset{(p\text{-Tol-})Ph.CO.CH_2S \cdot C \cdot SR}{\|}$$

$$\text{(I)} \qquad\qquad\qquad\qquad \text{(II)}$$
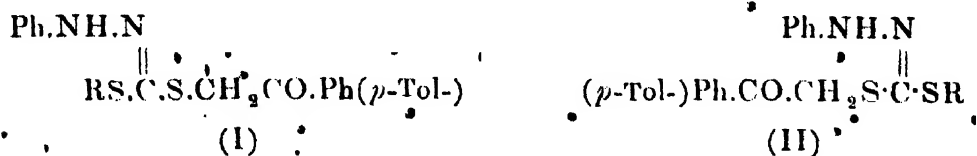
These assumptions receive indirect support from the melting points of the different isomerides as also from

their stability and behaviour towards phenylhydrazine. As already mentioned, the bright yellow products, for which the formula (I) has been assumed, readily yielded phenylhydrazones when boiled with phenylhydrazine in alcohol-acetic acid solution. The isomerides (II) on the other hand failed to do so. The non-formation of phenylhydrazones in the latter case is not abnormal if we assume a mutual influence of the keto and anilino groups due to their spatial proximity.

Attempts were made to obtain definite proof of these structures by experiment. It followed from the constitution (II) given above to the lower-melting isomerides that they would be converted into thiodiazine derivatives by the elimination of a molecule of water thus:

$$\underset{\underset{(p\text{-Tol-})Ph\cdot CO\cdot CH_2 S\cdot C\cdot SR}{\overset{\|}{Ph\cdot NH\cdot N}}}{}\xrightarrow{\quad H_2O \quad}(p\text{-Tol-})Ph\cdot C\begin{array}{c}Ph\\ |\\ N-N\\ \diagup \qquad \diagdown\\ CH-S\end{array}C\cdot SR$$

$$(III)$$
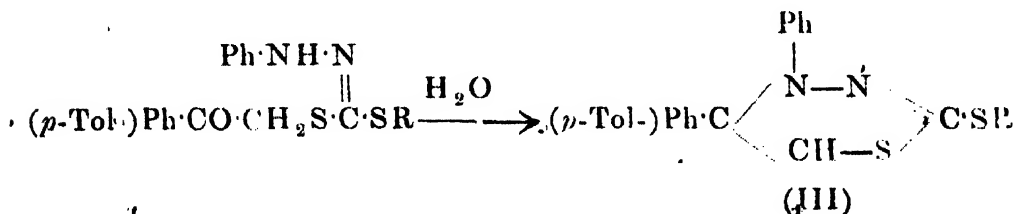
The higher-melting isomerides, represented by (I), on the contrary, are incapable of undergoing such intramolecular condensations due to the unfavourable positions of the reactive groups in the molecule. In actual experiment it was found, however, that both the isomerides, when heated to 100° in alcoholic solution for four hours or when heated without any diluent at 140-45° for 10-15 minutes yielded (III) with elimination of water. This result in the case of the *trans*-compound can be explained only on the assumption that (I) changes into (II)* before undergoing the thiodiazine condensation.

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* That such isomerides are interconvertible when kept in the fused state for some time has been observed by Busch. In the present case the transformation of (I) into (II) and *vice versâ* could be observed in many cases under suitable experimental conditions (*vide* pp. 211-12).

The production of thiodiazines by these methods is therefore not reliable for indicating the difference in constitution between (I) and (II).

Having failed to obtain the desired results under the experimental conditions mentioned above, attention was directed to observing the rate of elimination of water from the isomerides under strictly comparable conditions. For this purpose the isomerides of $Ph.NH·N : C·(SEt)·S·CH_2·CO·Ph$ were dissolved in anhydrous benzene containing a little anhydrous copper sulphate in suspension and the mixture was allowed to stand at the room temperature. It was expected that the copper sulphate would become blue much more quickly in the case of the cis-isomeride than in the other.

The compound, m. p. 87°, (for which a cis-structure has been assumed) gave after 48 hours a 45 per cent. yield of the corresponding thiodiazine. The development of the blue colour could not be observed as a portion decomposed into sulphuretted hydrogen thereby converting copper sulphate into cupric sulphide. The isomeride, m. p. 84° (for which a trans-configuration has been assumed), was found after the given period to have undergone partial isomeric change into the cis-compound. The copper sulphate in this case turned greyish but not blue. The thiodiazine was not formed at all even in the course of a week. This is certainly an unmistakable evidence in favour of the constitutions already proposed in the foregoing pages.

The thiodiazines can be obtained from either isomeride by the method already indicated. They may be directly obtained by boiling a mixture of the bromo-ketone and alkyl-phenyldithiocarbazinate in pyridine solution for a few minutes. The reaction, no doubt, proceeds with intermediate formation of the cis-compound. For it has been found that if the reaction in pyridine solution is

4

carried on at a low temperature a *cis*-compound is invariably obtained.

The *trans*-compounds, on the other hand, are also obtained when the reactants are boiled in alcoholic solution containing precipitated calcium carbonate in suspension. The function of the carbonate is to decompose the hydrobromic acid as soon as it is formed.

These reactions for the formation of *cis*-and *trans*-isomerides together with those mentioned in the beginning of the paper lead to the following conclusion.

An alkaline medium favours the formation of the *cis*-compound with the total exclusion of the *trans*-isomeride. A faintly acid medium, on the other hand, invariably yields the *trans*-compound.

The thiodiazines (III) are very stable substances with high melting points and form pale yellow, hard, transparent prisms or needles.

EXPERIMENTAL.

General Methods of Preparation of Phenacyl-alkyl-phenyldithiocarbazinates.

(*i*) Molecular proportions of alkyl-phenyldithiocarbazinate and ω-bromoacetophenone or *p*-methyl-ω-bromoacetophenone were dissolved in warm absolute alcohol, the solution rapidly cooled and one molecule of 10 per cent. alcoholic caustic potash or ammonia run in gradually with constant shaking. The precipitated potassium bromide was immediately filtered off: The filtrate deposited on standing yellow crystals which were purified by crystallisation from absolute alcohol. A rise of temperature during the reaction is undesirable as the yield is considerably diminished thereby.

(*ii*) Alkyl-phenyldithiocarbazinate (one mol.), the bromo-ketone (one mol.) and a large excess of precipitated

calcium carbonate (5-6 mols.) were heated in absolute alcoholic solution for 15-20 minutes, by which time the pungent smell of the bromo-ketone practically disappeared and the solution turned yellow. The solution was filtered and the filtrate on cooling yielded the dithioester in long bright yellow needles or plates which were found to be identical with the corresponding product obtained by the previous method.

These two methods yielded *trans*-phenacyl derivatives.

(*iii*). The alkyl-phenyldithiocarbazinate (1 mol.) was dissolved in alcoholic potash (1 mol. of 10 per cent.), the solution cooled and an alcoholic solution of one mol. of the bromo-ketone gradually added with constant shaking. The potassium bromide which had separated out, was immediately filtered off. The condensation product gradually separated from the filtrate in star-like aggregates which were collected after an hour, dried on porcelain and recrystallised from ligroin or dilute alcohol.

(*iv*). To a cold solution of the alkyl-phenyldithiocarbazinate (1 mol.) in pyridine, the solid bromo-ketone was added all at once and shaken thoroughly; the flask, in which the reaction was being carried out was kept cool. The reaction was completed within a few minutes. A large volume of water was then added when a brown oil was precipitated. The oil was dissolved in warm absolute alcohol. The alcoholic solution on standing for some time deposited pale yellow needles which were identical with the corresponding product obtained by method (*iii*).

The *cis*-compounds were formed by the last two reactions.

trans-*Phenacyl-methyl-phenyldithiocarbazinate,*

Ph.NH. N
$$\parallel$$
MeS·C·S·CH$_2$·CO·Ph
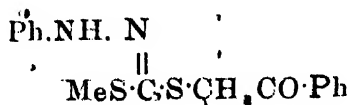
This compound was obtained by methods (*i*) and (*ii*). It crystallised from alcohol in bright yellow needles, m.p. 100°. It is extremely soluble in acetone, pyridine, chloroform and benzene and only sparingly soluble in light petroleum. The yield of the pure product amounted to about 80 per cent. of that required by theory. (Found: $C=60\cdot42$; $H=5\cdot48$. $C_{16}H_{16}ON_2S_2$ requires $C=60\cdot75$; $H=5\cdot33$ per cent.)

Phenylhydrazone.—The above ketone was heated in alcoholic solution under reflux for about 15 minutes with an excess of phenylhydrazine and a little acetic acid. The dark coloured solution was cooled, acidified with acetic acid and diluted with water when a brown oil separated. The oil solidified on being left overnight. After two crystallisations from a mixture of pyridine and alcohol it was obtained as colourless, hard prisms melting at 126-7°. The phenylhydrazone gradually turned brown on keeping. (Found: $N=13\cdot93$. $C_{22}H_{22}N_4S_2$ requires $N=13\cdot79$ per cent.)·

trans-*Phenacyl-ethyl-phenyldithiocarbazinate*, which was prepared like the preceding methyl derivative (90 per cent. yield), crystallised from hot alcohol in long, yellow needles, m. p. 82°. It is very soluble in acetone, carbon disulphide and pyridine but very sparingly in cold alcohol and hot ligroin. (Found: $C=61\cdot53$; $H=5\cdot37$; $N=8\cdot63$. $C_{17}H_{18}ON_2S_2$ requires $C=61\cdot81$; $H=5\cdot45$; $N=8\cdot48$ per cent.)·

The *phenylhydrazone*, obtained by the method already described, crystallised from dilute pyridine in transparent prismatic needles, m. p. 136°. (Found: $N=13\cdot41$. $C_{23}H_{24}N_4S_2$ requires $N=13.34$ per cent.)

n-*Propyl-phenyldithiocarbazinate.*—A mixture of $2\cdot7$ gm. of caustic potash in 30 c. c. of rectified spirit and 5 gm. of phenylhydrazine was cooled to 0° and 5 gm. of carbon disulphide were dropped in with constant shaking.

n-Propyl iodide (7·5 gm.) was added. The mixture was well shaken for some time and allowed to stand for an hour at the room temperature. 'The solution was then acidified with a very dilute solution of acetic acid. The crystals were collected, washed with water and recrystallised from dilute alcohol. Yield 5 gm. It formed colourless needles, m. p. 125°, which gradually decomposed on keeping. It is very soluble in benzene, acetone, pyridine, hot alcohol and aqueous alkali. (Found : N=12·34. $C_{10}H_{14}N_2S_2$ requires, N = 12·39 per cent.)

trans-*Phenacyl*-n-*propyl-phenyldithiocarbazinate*

$$\text{Ph·NH·N}$$
$$\|$$
$$C_3H_7S·C.S.CH_2COPh$$

was obtained by method (*ii*). It could not be obtained by method (*i*). It is very soluble in acetone, benzene, and ether and was crystallised from a small quantity of alcohol in yellow shining plates, m. p. 56°. (Found : N=8·22. $C_{18}H_{20}ON_2S_2$ requires N = 8·14 per cent.)

trans-*Phenacyl-benzyl-phenyldithiocarbazinate* could not be obtained either by method (*i*) or (*ii*).

trans-p-*Methylphenacyl-methyl-phenyldithiocarbazinate*, obtained by methods (*i*) and (*ii*) from equivalent quantities of *p*-methyl-ω-bromoacetophenone [1] and methyl-phenyldithiocarbazinate, crystallised from hot alcohol or

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[1] *Preparation of p-Methyl-ω-bromoacetophenone.*—To 26·8 gms. of *p*-methyl-acetophenone dissolved in 120 gms. of glacial acetic acid were added 30 gms. of bromine dissolved in 40 c. c. of the same solvent. The mixture was well shaken and heated in a warm water-bath at 50-60° for a few minutes until the red colour of bromine had completely disappeared. A current of dry air was passed through the solution to drive off the hydrobromic acid and the solution was poured on 400 gms. of crushed ice. After three hours the crystalline solid was collected under suction and recrystallised from rectified spirit. The yield of pure product amounted to about 60 per cent. of that required by theory.

The above procedure, which is a modification of Kunckell's method (*Ber.*, 1897, 30, 577), can be quickly carried out ; the product is purer and the yield better (60 per cent. as compared with 15 per cent. obtained by Kunckell's method).

dilute acetone in yellow shining plates, m. p. 109-110°. It is very soluble in benzene, carbon disulphide and pyridine but only sparingly in ligroin, ether and cold alcohol. (Found : C=61·53 ; H=5·47. $C_{17}H_{18}ON_2S_2$ requires C= 61·81 ; H=5·45 per cent.)

The *phenylhydrazone* crystallised from absolute alcohol in pale yellow star-like aggregates, m. p. 124·5°. (Found : N=13·38. $C_{23}H_{24}N_4S_2$ requires N=13·34 per cent.)

trans-p-*Methylphenacyl-ethyl-phenyldithiocarbazinate* prepared by method (*i*) or (*ii*), crystallised from absolute alcohol in sulphur-yellow plates, m. p. 95°. It is easily soluble in acetone, benzene, pyridine and chloroform but only sparingly in ligroin, ether and cold alcohol. (Found : N=8·23. $C_{18}H_{20}ON_2S_2$ requires N=8·14. per cent.)

cis-*Phenacyl-methyl-phenyldithiocarbazinate*

$$Ph·NH·N$$
$$\|$$
$$Ph·CO·CH_2S.C.SMe$$
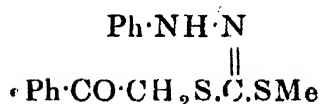
was obtained by methods (*ii*) and (*iv*) as pale yellow, slender needles. It was crystallised from dilute alcohol or ligroin. It was extremely soluble in most other organic media ; m. p. 93°. (Found : N=8·85. $C_{16}H_{16}ON_2S_2$ requires N=8·86 per cent.)

cis-*Phenacyl-ethyl-phenyldithiocarbazinate*, obtained by methods (*iii*) and (*iv*), crystallised in pale yellow, soft needles from ligroin, m. p. 86.° It was easily soluble in most organic media from which attempts to crystallise it were fruitless. (Found : C=61·31 ; H=4·49. $C_{17}H_{18}ON_2S^2$ requires C=61·81 ; H=4·45 per cent.)

cis-*Phenacyl-n-propyl-phenyldithiocarbazinate* was obtained by method (*iv*). From ligroin it separated in pale yellow, silky needles, m. p. 61°. (Found : N=8·28. $C_{18}H_{20}ON_2S_2$ requires N=8·14 per cent.)

The corresponding *benzyl* derivative, crystallised from

ligroin in long, pale yellow needles m. p. 75.° (Found: C = 66·94 ; H = 5·35. $C_{22}H_{20}ON_2S_2$ requires C = 67·34 ; H = 5·1 per cent.)

cis-p-*Methyl-phenacyl-methyl-phenyldithiocarbazinate*

$$Ph·NH·N$$
$$\|$$
$$Me·C_6H_4CO·CH_2S.C.SMe$$
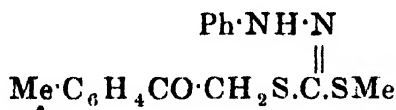
prepared by methods (iii) and (iv), from methyl-phenyl-dithiocarbazinate, and p-methyl-ω-bromoacetophenone, crystallised from ligroin in star-like aggregates, m. p. 54°, and was highly soluble in most organic solvents. (Found : N = 8·60. $C_{17}H_{18}ON_2S_2$ requires N = 8·49 per cent.)

cis-p-*Methyl-phenacyl-ethyl-phenyldithiocarbazinate* obtained in an analogous manner formed very pale yellow needles, m. p. 76-77.° It was highly soluble in most organic media. (Found : N = 8·20. $C_{18}H_{20}ON_2S_2$ requires N = 8·14 per cent.)

2-Methylthiol-4 : 5-diphenyl-1 : 3 : 4-thiodiazine.
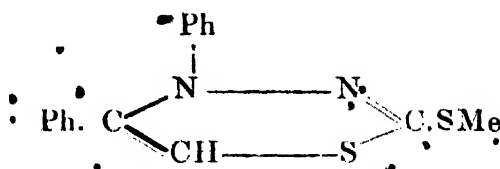
Methylphenyldithiocarbazinate (2 g.) was dissolved in 5 c.c. of pure pyridine, an equal weight of ω-bromoacetophenone added, and the solution was then boiled for about three minutes. The reaction-mixture was poured into water when an oil separated. The oil was dissolved in hot absolute alcohol and allowed to cool. A pale yellow crystalline precipitate (1·15 g.) was obtained. After two or three recrystallisations from a mixture of pyridine and alcohol, the thiodiazine was obtained as pale yellow, hard prisms, m. p. 180°. It was sparingly soluble in alcohol, acetone or benzene but easily in pyridine: (Found:

C = 64·42; H = 4·66. $C_{16}H_{14}N_2S_2$ requires   C = 64·43; H = 4·70 per cent.)

2-*Ethylthiol*-4 : 5-*diphenyl*-1 : 3 : 4-*thiodiazine* was obtained from molecular proportions of ethyl-phenyldithiocarbazinate and ω-bromoacetophenone in an analogous manner. It was found to be easily soluble in benzene, carbon disulphide and pyridine and separated from a mixture of pyridine and alcohol in pale yellow, transparent prisms, m. p. 150°. (Found: C = 65·12; H = 5·27. $C_{17}H_{16}N_2S_2$ requires   C = 65·37; H = 5·13 per cent.)   The corresponding *n*-propyl- and benzyl-thiol-thiodiazines could not be obtained by this method.

Conversion of cis-*Phenacyl-methyl-phenyldithiocarbazinate into* 2-*Methylthiol*-4: 5-*diphenyl*-1: 3: 4-*thiodiazine.*

(*a*) One gm. of the *cis*-compound in 25 c.c. of absolute alcohol was heated in a sealed tube for four hours at about 100°. The cold alcoholic solution slowly deposited pale yellow crystals of the thiodiazine which, when purified, melted at 180°. A mixture of this compound and that obtained by the previous method had the same melting point. The corresponding *trans*-compound, under the same conditions, also underwent conversion into the same thiodiazine.

(*b*) The condensation was also effected by heating the *cis*- or *trans*-compound for 15-20 minutes at 140-45°. Water was eliminated; a little sulphuretted hydrogen was also noticed. The pasty mass was dissolved in a small quantity of pyridine, diluted with a large excess of alcohol and set aside for several days. The thiodiazine crystallised out very slowly in transparent prisms which were purified by repeated recrystallisation from a mixture of pyridine and alcohol. The pure product melted at 179-80° and its identity with 2-methylthiol-4:5-diphenyl-1:3:4-thiodiazine was established by the usual methods.

2-Ethylthiol-4 : 5-*diphenyl*-1 : 3 : 4-*thiodiazine* was similarly obtained from *cis-* and *trans*-phenacyl-ethyl-phenyldithiocarbazinate. ·

2-n-*Propylthiol*-4 : 5-*diphenyl*-1 : 3 : 4-*thiodiazine* was prepared according to the method (*b*), given above. It separated from a mixture of pyridine and alcohol in almost white microscopic needles, m. p. 150-151°. (Found:· C = 66·24 ; H = 6·07. $C_{18}H_{18}N_2S_2$ requires C = 66·27 ; H = 5·52 per cent.)

2-*Methylthiol*-4-*phenyl*-5-*p-tolyl*-1 : 3 : 4-*thiodiazine* was obtained from *trans-p*-methylphenacyl-methyl-phenyldithiocarbazinate by method (*a*). It crystallised from a mixture of pyridine and alcohol in golden yellow, shining plates, m. p. 187°. (Found: C = 65·19 ; H = 5·18. $C_{17}H_{16}N_2S_2$ requires C = 65·37 ; H = 5·13 per cent.) The *cis*-compound, however, when heated at 100° for three hours in alcoholic solution, yielded the corresponding *trans*-isomeride, m. p. 110°. The thiodiazine was not formed.

Isomeric Transformation of p-*Methylphenacyl-ethyl-phenyldithiocarbazinates.*

The *cis*-compound (1 g.) dissolved in 25 c.c. of alcohol was heated at 100° for four hours in a sealed tube. On concentration of the solution a mixture of the isomerides was obtained. These were collected, dried in the air and the isomerides separated by taking advantage of the greater solubility of the *cis*-compound in petroleum ether. The *trans*-compound, under similar conditions, alas yielded a mixture of the two isomerides. Evidently the reaction is reversible, thus :

$$\text{Ph.NH.N} \quad \rightleftarrows \quad \text{Ph.NH.N}$$
$$\text{Me·C}_6\text{H}_4\text{·CO.CH}_2\text{S.C.SEt} \qquad \text{EtS.C.S.CH}_2\text{CO.C}_6\text{H}_4\text{·Me}$$
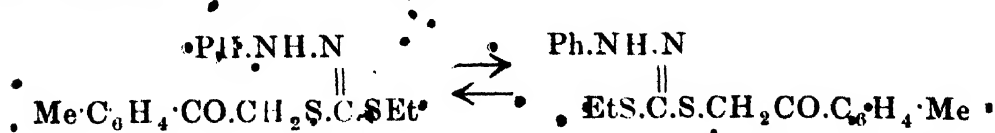
At a higher temperature (120-30°) intramolecular condensation took place with the formation of 2-*ethylthiol*-4-*phenyl*-5-*p-tolyl*-1 : 3 : 4-*thiodiazine*. The thiodiazine

5·

crystallised from a mixture of pyridine and alcohol in pale yellow, compact needles or prisms, m. p. 148°. (Found; C = 66·11; H = 5·65. $C_{18}H_{18}N_2S_2$ requires C = 66·27; H = 5·52 per cent.)

Constitution of the Isomerides of Phenacyl-ethyl-phenyl-dithiocarbazinate.

cis-Phenacyl-ethyl-phenyldithiocarbazinate   (0·4 g.) was dissolved in 10 c.c. of anhydrous benzene. A little anhydrous copper sulphate was added and the mixture was allowed to stand at the room temperature. The copper sulphate gradually turned brown and ultimately black due to the formation of cupric sulphide. After 48 hours, the mixture was filtered and the filtrate was evaporated. The dark coloured oil left behind was washed with ligroin. It hardened in the course of several hours and was twice recrystallised from a mixture of pyridine and absolute alcohol. The product, pale yellow needles m. p. 150°, was found to be identical with 2-ethylthiol-4 : 5-diphenyl-1 : 3 : 4-thiodiazine (*vide* p. 210). The yield was about 45 per cent.

trans-Phenacyl-ethyl-phenyldithiocarbazinate, under similar conditions, gave, after removal of benzene, a mixture of the original compound together with a little of the *cis*-isomeride. There was practically no improvement even when the solution was allowed to stand for a week.

I desire to convey my thanks to Sir P. C. Rây for his interest and encouragement during the course of the investigation.

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A Note on the Variable Tannin Content of the Wood of the Kumaon Oak

(Quercus incana).

By

H. S. CHATURVEDI AND E. R. WATSON.

We became interested in the tannin content of the wood of the Kumaon oak when we found that the bark alone is not available in sufficiently large quantities to make a commercial proposition of the manufacture of tannin extract from that material.

Pilgrim (*Indian Tanstuffs*, 1920) found 4·91 per cent. tannin, 4·27 per cent. soluble non-tannins in a sample of the wood supplied by the Inspector General of Forests, Simla. In a preliminary examination of a small sample supplied by Mr. Gill, from Ramgarh, near Nainital, we found about 3 per cent. tannin and 2 per cent. non-tannin, and colour about 3·3 times as dark as decolourised French chestnut extracts. We then obtained about 20 maunds of the wood through the Divisional Forest Officer, Nainital. This was supplied from Bhowali (near Nainital) in March and on analysis gave only 0·8 per cent. tannin, 3·7 per cent. soluble non-tannins and 20·2 yellow, 14·0 red (colour in 1 cm. tube for 0·5 per cent. tannin content).

One of us paid a visit to the Nainital district in November and selected samples, from Bhowali and

Ramgarh, of young and old trees, main stems and branches : these on analysis gave the following results :—

Sample.	Moisture.	Tannin.	Soluble non-tannin.	Colour.	
				Yellow.	Red.
Young stem (Ramgarh)	9·1	3·6	3·9	10·5	7·0
Young stem (Bhowali)	9·6	1·9	4·2	7·1	5·2
Mature stem (Ramgarh)	16·6	3·3	2·7	8·6	6·4
Mature stem (Bhowali)	8·6	3·6	5·7	14·6	8·7
Mature branches (Ramgarh)	7·1	4·2	3·9	10·7	6·5
Mature branches (Bhowali)	10·4	3·5	5·6	12·1	7·1
Young branches (Ramgarh)	8·6	3·8	2·4	10·9	5·9
Young branches (Bhowali)	9·1	3·2	4·1	8·4	5·0

A consignment of 1 ton was then ordered from the Forest Ranger, Bhowali, who had supplied the previous consignment and had helped us in getting samples in November. He supplied wood from the main stem and branches of old trees from Ramgarh and to our great disappointment this on analysis gave

	Total soluble matter.	Tannin.	Soluble non-tannin.	Colour.	
				Yellow.	Red.
(a)	3·7	1·5	2·2	28·3	15·7
(b)	4·2	1·7	2·5	30·4	18·0

This consignment was supplied in August.

Evidently the percentage of tannin in the wood varies in a most capricious manner and considering that the tannin is always on the low side, the wood does not seem worth further consideration as a source of tannin extract.

The Oxidizing Action of Alkaline Ferricyanide and the Composition of Higher Oxides of Cobalt.

By

DAYANANDA BHADURI AND PRIYADARANJAN RÁY.

Potassium ferricyanide in alkaline solution has been used extensively as an oxidizing agent and its use has led to the development of many important analytical methods. The present work was undertaken in order to investigate its oxidizing action upon cobalt and nickel salts, the constitution of their higher oxides, and the possibility of establishing a rapid volumetric method for their estimation.

A number of higher oxides of cobalt have been described, viz., Co_2O_3, Co_3O_5, Co_3O_4, Co_4O_5, Co_6O_7, Co_7O_{11}, Co_8O_9 and CoO_2. It is extremely doubtful whether all of them have separate existence: most of them are simply mixtures of two or more definite oxides. It is also quite possible that different oxidizing agents behave differently towards solutions of cobalt and nickel salts leading to products of different compositions. Lately, however Howell has thoroughly studied the constitution of the higher oxides of cobalt (*J. Chem. Soc.*, 1923, 123, 65) and of nickel (*J. Chem. Soc.*, 1923, 123, 669; 1772) obtained by the action of alkaline hypochlorite solutions. In the case of cobalt the only definite oxide obtained by him was Co_2O_3. In the case of nickel the oxide, Ni_2O_3 and an unstable peroxide, NiO_2 were obtained. The action of alkaline ferricyanide upon cobalt salts, which forms the

subject of the present paper, indicates, however, the exis·tence of Co_3O_4 and Co_2O_3 as definite oxides and a higher one of the peroxide type. Nickel, on the other hand, was found to be very little affected by alkaline ferricyanide showing that it is much less easily oxidized than cobalt.

The oxidizing action of potassium ferricyanide depends upon the fact that, in alkaline solution in the presence of an oxidizable substance, it is reduced to ferrocyanide. Kassner (*Arch. Pharm.*, 1896, *235*, 330) studied the behaviour of the ferricyanides as oxidizing agents, the nature of the oxidation and the conditions under which they can be used to best advantage. He found that potassium ferricyanide solution when mixed with potassium hydroxide solution, was stable in the dark at low temperatures only; when heated to above 60° or exposed to direct sunlight, it was partially decomposed, ferric hydroxide was deposited and the solution contained ammonia and cyanide. When alkali carbonate was substituted for the hydroxide the extent of the decomposition was considerably less and was reduced still further when an alkali bicarbonate was employed. According to him a permanent ferricyanide solution bath for oxidizing and bleaching purposes can be maintained in the dark at a temperature below 60°. But the decomposition of the reagent itself under the conditions of experiments described in this paper has been shown to be negligibly small and not seriously to affect the results of a quantitative study of the reactions.

EXPERIMENTAL.

Stability of Alkaline Ferricyanide Solution.

Three small beakers were taken. The first contained a strongly alkaline solution of potassium ferricyanide;

the second, the same solution in contact with a filter paper; the third, an alkaline solution of potassium ferrocyanide. All were left exposed to the air, and, after 45 minutes, portions from each of them were tested. No ferrocyanide was detected in the first solution; only a green colouration with acidified ferric-alum solution was obtained in the second solution and the third gave no test for ferricyanide. This proves that alkaline ferricyanide solution alone, in the absence of direct sunlight is fairly stable to air and if any change takes place at all it must be very slow. In the presence of organic matter like filter paper a slight decomposition occurs which can also be neglected for all practical purposes in such rapid analytical operations as were followed in the present investigation.

Procedure.

An alkali solution was prepared and the strength was daily determined with a standard acid solution. A solution of $N/20 \cdot KMnO_4$ was prepared and its strength was determined against chemically pure potassium ferrocyanide. Crystals of "Merck's Reagent" potassium ferricyanide were washed and dissolved in water. The solution was made up to a definite volume and its strength determined daily against the permanganate solution. A solution of "Merck's Reagent" potassium hydroxide was made and the amount of KOH and K_2CO_3 per c.c. of the solution was determined daily.

Two series of experiments were performed. In the first, the amount of alkali was kept constant while the amount of ferricyanide was progressively increased; in the second, the alkali was gradually increased while the amount of ferricyanide was kept constant. In the first series the amount of alkali employed was in excess of that required for the precipitation of all the cobalt as cobalt

hydroxide and for the complete oxidation of the latter to the $\overset{0}{C}oO_2$ stage. In the second series, the amount of ferricyanide used was in excess of that necessary for the complete oxidation of all the cobalt to the CoO_2 stage. The estimations were then carried out in the following manner. A definite volume of chemically pure nickel-free cobalt nitrate solution containing a known amount of cobalt was run into a beaker from a burette and made up to 50 c.c. with water. Standard ferricyanide solution was run from a burette into a measuring cylinder containing the required amount of alkali previously introduced into it from another burette and made up to 100 c.c. with water. This was then slowly added to the cobalt solution with continuous stirring. The cylinder was washed with another 100 c.c. of water and the latter was added to the cobalt solution thus making the total volume up to 250 c.c. The mixture was then thoroughly stirred with a mechanical stirrer for about half an hour and transferred to a 500 c.c. measuring flask, the beaker was well washed, and the washings also added to the liquid in the flask. Water was then added up to the mark and the flask thoroughly shaken. The solution was filtered through a dry filter paper; first 20—25 c.c. of the filtrate were rejected and then 100 c.c. of the filtrate were acidified with dilute sulphuric acid and titrated with $KMnO_4$ solution. Table I gives the results of the first series of experiments. These results have been plotted on a curve in Fig I. The equivalent amounts on the graph are calculated on the basis of the amount of cobalt taken as unit equivalent. Thus one equivalent of available oxygen is the amount necessary for the conversion to Co_2O_3 of all the cobaltous oxide corresponding with the amount of the cobalt salt taken. The equivalents of alkali and ferricyanide have also been represented on the same basis. In the case of the alkali, however, a necessary deduction has
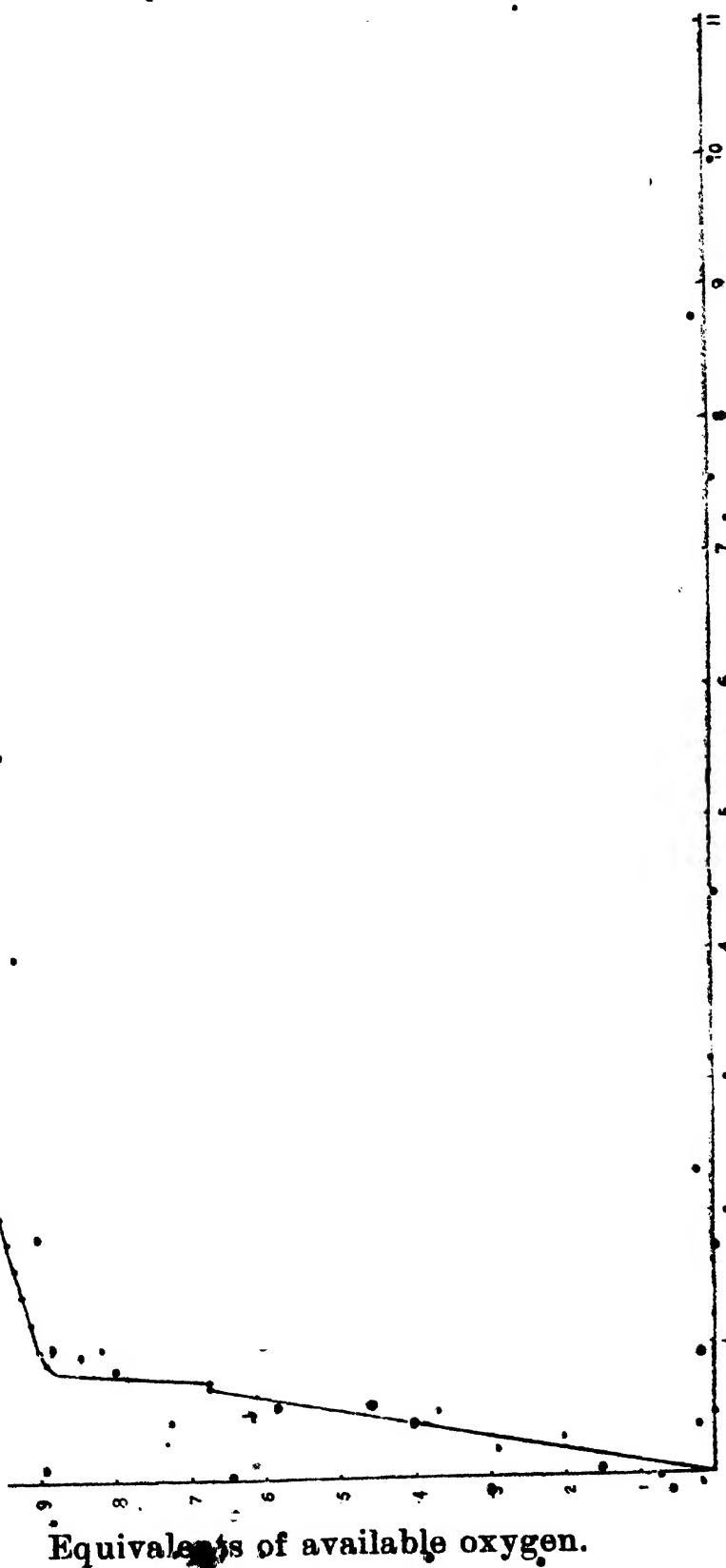
Equivalents of Pótassiam ferricyanide.

Fig. I

Equivalents of available oxygen.

been made for the precipitation of the cobalt as hydroxide from the solution of its salt.

TABLE I.
Cobalt taken = 0·09 gm.

KOH	K₂CO₃	Total alkali.	Potassium ferri-cyanide.	Equivalents of available oxygen.
0·7376 g.	0·0199 g.	0·7575 g.	0·15 g. = 0·2986 eqv.	0·2852
0·7376	0·0257	0·7624	0·20 = 0·3981 ,,	0·3820
0·7370	0·0206	0·7576	0·26 = 0·5175 ,,	0·5100
0·7370	0·0206	0·7576	0·335 = 0·6670 ,,	0·6690
0·7387	0·0153	0·7540	0·38 = 0·7564 ,,	0·6690
0·7370	0·0206	0·7576	0·45 = 0·8958 ,,	0·8920
0·7387	0·0153	0·7540	0·50 = 0·9953 ,,	0·9000
0·7387	0·0153	0·7540	0·60 = 1·1944 ,,	0·9160
0·7370	0·0206	0·7576	0·70 = 1·3935 ,,	0·9240
0·7370	0·0206	0·7576	0·80 = 1·5924 ,,	0·9320
0·7370	0·0206	0·7576	0·90 = 1·7916 ,,	0·9400
0·7370	0·0206	0·7576	1·00 = 1·9905 ,,	0·9480
0·7370	0·0206	0·7576	1·35 = 2·6874 ,,	0·9720
0·7370	0·0206	0·7576	2·00 = 3·9810 ,,	0·9580
0·7370	0·0199	0·7575	3·00 = 5·9718 ,,	0·9960
0·7376	0·0199	0·7575	4·00 = 7·9624 ,,	1·0040
0·7367	0·0221	0·7588	5·00 = 9·9530 ,,	1·0600
0·7367	0·0221	0·7588	6·00 = 11·9440 ,,	1·0600
0·7374	0·0262	0·7636	7·00 = 13·9350 ,,	1·0680

Discussion of Results obtained in the First Series of Experiments.

It will be observed from the curve that when the alkali-strength is kept constant (about 6·64 equivalents), an increase in the amount of available oxygen in the oxide formed occurs with an increasing amount of ferri-

6

cyanide. The increase in the first four experiments is very rapid. After this there is a break or arrest in the curve corresponding with the composition, Co_3O_4 (oxygen equivalent $= 0.66$). Then the available oxygen increases rapidly to a point slightly below the composition of Co_2O_3 and subsequently slowly to Co_2O_3. Here it remains practically constant at about 1.06 equivalent of available oxygen even with further increase in the amount of ferricyanide added. The final product obtained is therefore practically pure Co_2O_3, slightly peroxidized. From the nature of the curve it is apparent that no direct peroxidation of cobalt occurs under these conditions. The cobaltous oxide is first oxidized to Co_3O_4 and then to Co_2O_3; six to eight equivalents of ferricyanide were actually required to carry the oxidation to Co_2O_3, even in the presence of an excess of alkali. Theoretically, one equivalent of ferricyanide with one equivalent of alkali can carry the oxidation to Co_2O_3 and two equivalents of ferricyanide with two equivalents of alkali are sufficient for oxidation to the CoO_2 stage. The results, therefore, indicate that the reaction does not proceed to completion in the sense of the following equation :—

$$2Co(OH)_2 + 2KOH + 2K_3Fe(CN)_6 = Co_2O_3 + 2K_4Fe(CN)_6 + 3H_2O.$$
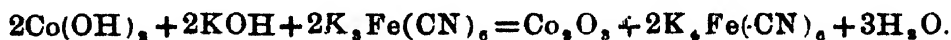
In fact, the maximum degree of oxidation experimentally realized even with a very large excess like fourteen equivalents of ferricyanide was only slightly above Co_2O_3 (1.065 equivalents of available oxygen). It shows that as the degree of oxidation increases, the system tends to oppose further oxidation. This could not be due to any coating of a higher oxide over the next lower one thus preventing further oxidation, as the mixture in every case was thoroughly stirred with a mechanical stirrer for a definite period. On the other hand oxidation to Co_3O_4 becomes complete with a requisite

Equivalents of available oxygen.

Equivalents of alkali.
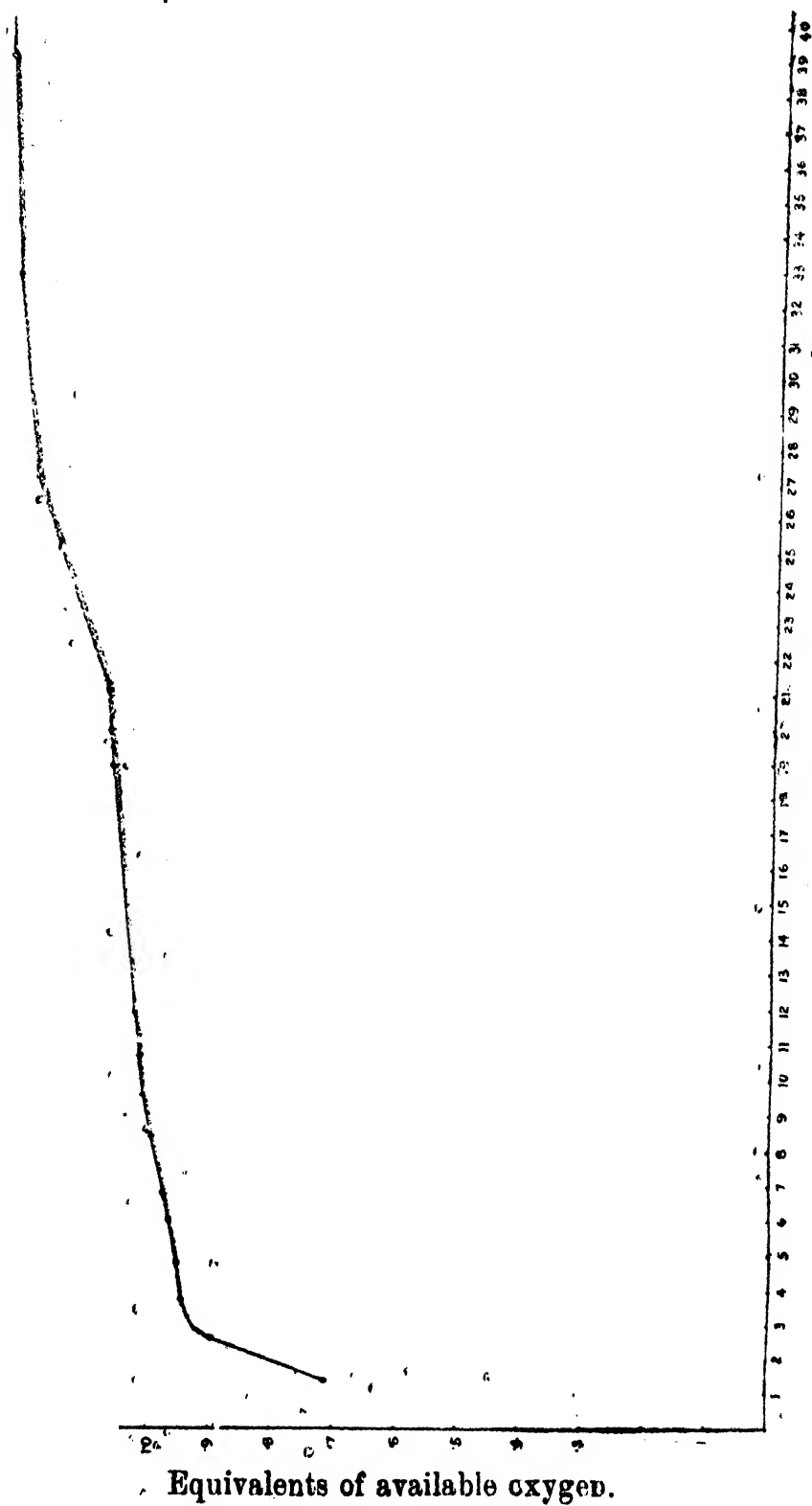
Fig. II.

theoretical amount of ferricyanide (=0·67 equivalent), according to the equation :—

$$3Co(OH)_2 + 2KOH + 2K_3Fe(CN)_6 = Co_3O_4 + 2K_4Fe(CN)_6 + 4H_2O.$$
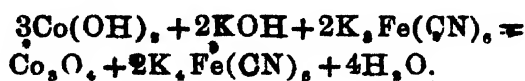
The second series of experiments (Table II, Fig. II) was performed in the same manner as the first: the amount of potassium ferricyanide (3·6 equivalents) was kept constant, while the amount of alkali was gradually increased.

TABLE II.
Cobalt taken = 0·09 gm.

KOH		K₂CO₃ in grams.	Total alkali in grams.	Potassium ferricyanide		Equivalents of available oxygen.
in grams	in equivalents.*			in grams	in equivalents.	
0·3009	1·515	0·0087	0·3096	1·8	3·6	0·7090
0·4005	2·679	0·0116	0·4121	,,	,,	0·8920
0·5000	3·841	0·0146	0·5746	,,	,,	0·9400
0·5996	5·005	0·0168	0·6164	,,		0·9480
0·6992	6·168	0·0194	0·7188	,,		0·9640
0·7545	6·814	0·0219	0·7764	,,		0·9720
0·8983	9·494	0·0260	0·9243	,,		0·9880
0·9978	9·656	0·0290	1·0269	,,		0·9960
1·0974	10·820	0·0319	1·1293	,,		1·0040
1·1970	11·984	0·0348	1·2318	,,		1·0120
1·7960	18·981	0·0520	1·8480	,,		1·0480
2·0007	21·375	0·0541	2·0548	,,		1·0520
2·5037	27·249	0·0676	2·5713	,,		1·1630
3·0023	33·074	0·0811	3·0834	,,		1·1870
3·9900	44·612	0·1414	4·1304	,,		1·2110
4·9875	56·791	0·1755	5·1630	,,		1·2210

* Equivalents of alkali have been calculated by subtracting 0·1712 gm. in each case, for this amount of alkali was required to precipitate the cobalt as Co(OH)₂ from the solution and so played no part in the oxidation of the cobaltous hydroxide.

Discussion of Results Obtained in the Second Series of Experiments.

Here rapid oxidation occurs up to a point slightly below the composition of Co_2O_3 then the rate slows down but as far as it has been investigated the oxidation proceeds continually through Co_2O_3 to a peroxidized state corresponding with $1\cdot22$ equivalents of available oxygen. As in the previous series, no direct peroxidation occurs. It can therefore be concluded that in the presence of an excess of alkali the extent of oxidation is increased, other conditions remaining unaltered. Peroxidation becomes prominent in this case only with $3\cdot6$ equivalents of ferricyanide. Oxidation to the Co_2O_3 stage with this amount of ferricyanide is effected with about eleven equivalents of alkali.

In Fig. II, as in Fig. I, a bend occurs at about $0\cdot9$ equivalents of available oxygen, that is a little below the composition of Co_2O_3. Then the degree of oxidation increases steadily but at a much slower rate to beyond the Co_2O_3 stage. Hence it is apparent that the preparation of pure Co_2O_3 in presence of a very large excess of alkali by the addition of ferricyanide would be very difficult. The product in that case would probably consist of a mixture of Co_2O_3 with either a still higher oxide like CoO_2 or a lower oxide like Co_3O_4. Here also as in the first series the oxidation is never quantitative. Excess of alkali, however, raises the oxidizing potential or capacity of ferricyanides to a certain extent. Two series of experiments in which the reaction was allowed to proceed to completion were then performed to ascertain the influence of the concentration of the reacting substances upon the results obtained. The results (Table III) show that the concentrations of the reacting substances have no influence on the results obtained.

TABLE III.

Cobalt taken $= 0 \cdot 09$ gm.

	KOH.	K_2CO_3.	Total alkali.	$K_3Fe(CN)_6$	Volume.	Equivalents of available oxygen.
First Series.	0·9978 g.	0·0290 g.	1·0268 g.	1·8 g.	125 to 500 c.c.	0·996
Second Series.	1·1895 g.	0·0322 g.	1·2217 g.	,,	125 c.c.	1·012
	,,	,,	,	,,	250 ,,	1·013
	,,	,,	,,	,,	500 ,,	1·008

The influence of temperatures below that of the decomposition of alkaline potassium ferricyanide solution upon the final results was then studied. The reacting solutions were brought to the required temperature before mixing. Then they were mixed and the reaction was allowed to proceed to completion at the same temperature (thermostat). The results (Table IV) show that temperature has no influence on the final results obtained, provided it is not very near that of the decomposition of potassium ferricyanide solution.

TABLE IV.

Cobalt taken $= 0 \cdot 081$ gm.; alkali $= 0 \cdot 67$ gm.; $K_3Fe(CN)_6 = 6 \cdot 3$ gm.

Temperature °C.	Available oxygen calculated from the results in Table 8.	Available oxygen found.
0°—42°	0·1098 gm.	0·11 gm.

The following results (Table V) show that the degree of oxidation, as determined by the estimation of ferrocyanide in the filtrate, is very little affected by the time of contact of the precipitated oxide with the solution. In these experiments no time was allowed for stirring the mixed solution. Corresponding results obtained with stirring are also placed side by side for comparison.

TABLE V.

Cobalt taken = 0·09 gm.

KOH.	K₂CO₃.	Total alkali.	Ferricyanide.	Available oxygen without stirring.	Available oxygen with stirring.
2·0007 g.	0·0541 g.	2·0548 g.	1·8 g.	0·0127 g.	0·0126; 0·0128
2·5037	0·0676	2·5713	1·8 g.	0·0143	0·0142
3·0023	0·0811	3·0834	1·8 g.	0·0145	0·0144; 0·0145

It has already been indicated in Table II that slight peroxidation occurs above a certain concentration of alkali when the amount of ferricyanide remains constant. The above experiments in Table V correspond with the conditions which give rise to the formation of this peroxidized product. Hence these results show that the reagent is not affected catalytically to any appreciable extent by the decomposition of the peroxide formed, though the latter may undergo some decomposition by long stirring or keeping, as indicated by the results recorded in Table VI.

In a set of experiments the results of which are recorded in Table VI both the filtrate and the precipitated

oxide were analysed. It will be observed that in the first
three experiments the available oxygen found in the
precipitate is less than that calculated from the filtrate.
The oxide CoO_2 is decomposed by water and the low value
of oxygen in the precipitate was possibly due to the
decomposition of the peroxide by the washing necessary
to free it from ferricyanide ; when no peroxidation can
possibly occur, the two values agree closely (*vide* Table
VI, Expt. 4)

TABLE VI.

Cobalt taken $= 0 \cdot 09$ gm.

KOH	K_2CO_3	Total Alkali.	Ferricya-nide.	Equivalent of available oxygen	
				from the filtrate.	in the pre-cipitate.
2·0007 g.	0·0541 g.	2·0548 g.	1·8 g.	1·049	0·95
2·5037 ,,	0·0676	2·5713	,,	1·164	1·061
3·0023	0·0811	3·0834	,,	1·18	1·083
0·0387	0·0153	0·7540	0·39	0·795	0·788

The presence of nickel salts beyond a certain
concentration and iron salts in general give low results and
retard the oxidation of cobalt even when the amount of
alkali is sufficient for the oxidation of cobalt to the
Co_2O_3 stage, allowing for what is required for the precipita-
tion of nickel and iron as their hydroxides. This is
evident from Tables VII, VIII and IX.

TABLE VII.

Cobalt taken	Nickel added.	Available oxygen found.	Available oxygen without nickel.
0·996 g.	0 0186 g.	0·01327 g.	0·0130 g.
	0·0273	0·0130	
	0·0409	0 0129	,,
	0·0682	0 0124	,,
	0 0954	0·0108	,,

TABLE VIII.

Cobalt taken.	Iron added.	Available oxygen found.	Available oxygen without iron.
0 948 g	0·0045 g	0 0064 g.	0·0065 g.
	0·0111	0 0063	
	0·0222	0·005?	
	0·0333	0·0047	

TABLE IX.

Cobalt taken.	Iron added.	Alkali.	Ferricyanide	Available oxygen found.	Available oxygen without iron.
0 048 g.	0 0222 g.	0·8930 g.	7·2 g.	0·0054 g.	0·0065 g.
,,	,,	1·1208	8·9	0·0060	,,
,,	,,	1·3475	10·8	0·0068	,,
,,	,,	1·5668	12·0	0·0064	,,

From the last table it will be observed that in presence of iron a very large excess of the reagent mixture is necessary to oxidize the cobalt to Co_2O_3 stage.

An attempt was also made to study the constitution of higher oxides of nickel by oxidation with alkaline ferricyanide. Two higher oxides, Ni_2O_3 and NiO_2 have been described by earlier workers. Howell (*loc. cit.*) has definitely established that by oxidation with alkaline hypochlorite solution the two oxides NiO_2 and Ni_2O_3 are formed simultaneously, that the former is unstable and decomposes readily to NiO, and that the sesquioxide is not oxidized directly to the peroxide.

The oxidation of nickel by alkaline ferricyanide was studied in exactly the same manner as in the case of cobalt ; chemically pure nickel free from cobalt was employed Tables X and XI indicate the results obtained.

TABLE   X.

Nickel used = 0·046 gm.

KOH	K_2CO	Total alkali	$K_3Fe(CN)_6$	Equivalents of available oxygen
0·6235 g	0·0100 g.	0·6335 g	0·14 g	0·0129
,,	,,	,,	0·28 ,,	0·0172
,,	,,	,,	0·84 ,,	0·0215
,,	,,	,,	1·54 ,,	0·0258
,,	,,	,,	2·38 ,,	0·0387
,,	,,	,,	3·38 ,,	0·0430
,,	,,	,,	4·62 ,,	0·0473
,,	,,	,,	6·16 ,,	0·0645
,,	,,	,,	7·14 ,,	0·0730

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·Table XI.

Nickel used = 0·0846 gm.

KOH.	K_2CO_3	Total alkali.	$K_3Fe(CN)_6$	Equivalents of available oxygen.
0·7521 g.	0·0121 g.	0·0642 g.	1·7 g.	0·0300
1·2663 ,,	0·0203	1·2366	,,	0·0344
1·9091 ,,	0·0306	1·9397	,,	0·0430
3·1947 ,,	0·0512	3·2459	,,	0·0730
4·4803	0·0718	4·5521	,,	0·0817

Equivalents of available oxygen have been calculated on the basis of nickel used; unit equivalent being the stoichiometric amount necessary for the conversion of all the NiO to the sesquioxide Ni_2O_3.

From the above data it becomes apparent that with a constant amount of alkali, the amount of available oxygen increases very slowly with the increasing amount of ferricyanide, though the actual amount is very low. Similarly, with a constant quantity of ferricyanide, increasing the quantity of alkali raises the available oxygen-content of the precipitate. Here also the actual amount of increase in the available oxygen-content is very small, though the rate of increase is somewhat more rapid than in the previous case. With a very large constant excess of potassium ferricyanide the extent of oxidation increased at a greater rate than is indicated in Table XI, but in all these cases the extent of oxidation was very small.

It can therefore be concluded that nickel is much less easily oxidizable than cobalt. In other words, for the same equivalent amounts of nickel and cobalt, a greater concentration of a given oxidizing agent is

required for nickel. The concentration of alkaline ferri-cyanide which oxidizes cobalt to the sesquioxide Co_2O_3, fails to form a higher oxide of nickel.

Summary.

(1). Alkaline ferricyanide under certain conditions can oxidize cobaltous hydroxide readily and quantitatively to Co_3O_4. Rapid oxidation proceeds up to a little below Co_2O_3 then further oxidation progresses extremely slowly. The oxidation of cobaltous hydroxide is gradual and progressive. No direct peroxidation or simultaneous formation of two higher oxides from $Co(OH)_2$ has been detected. The formation of two definite oxides Co_3O_4 and Co_2O_3 has been established and that of a peroxide, CoO_2 indicated.

(2). Other factors remaining unchanged, alkali in-creases the extent or degree of oxidation. With very large excess of alkali appreciable peroxidation occurs.

(3). Under certain conditions, with a limited amount of alkali and excess of ferricyanide, practically pure Co_2O_3 can be obtained.

(4). Temperatures up to 42° C and variation of the concentrations of the reacting solutions have no effect upon the character of the product obtained.

(5). The time of contact of the precipitate with the oxidizing solution has no effect upon the nature of the final product up to the Co_2O_3 stage. Peroxidized cobalt loses a part of its oxygen as shown in Table VI, but the alkaline ferro- or ferri-cyanide is not affected in any way thereby (Table V).

(6). The presence of nickel salts beyond a certain concentration and iron salts in general appears to retard the oxidation of cobalt.

(7). Even with a large excess of alkali and ferricyanide only a very small fraction of nickel is oxidized.

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The Recovery of Sucrose from Cane-sugar Molasses.

BY

E. R. WATSON, K. C. MUKERJEE, THE LATE D. N. GUPTA AND H. S. CHATURVEDI.

It is well known that a considerable quantity of sucrose remains in molasses, being prevented from crystallising by the presence of other substances. Sucrose is recovered on a commercial scale from beet-sugar molasses by precipitating the difficultly soluble strontium sucrate, which is collected, washed and decomposed by carbonic acid, which precipitates strontium carbonate and liberates pure sucrose in solution; or more economically by the Steffen process which uses lime instead of strontia, and precipitates the difficultly soluble tricalcium sucrate. In practice the tricalcium sucrate is never decomposed by carbonic acid directly but is added to fresh juice, instead of its equivalent of lime, and is decomposed in the carbonation process, so that the sucrose recovered from the molasses is added to a following batch of juice. The authors have never seen any data as to the yield and purity of sucrose recoverable from beet-sugar molasses by the Steffen process. The authors are informed by Mr. Noel Deerr that in Europe nearly all sugar factories are equipped for the Steffen process and that whether the molasses is treated by this process or sold for the manufacture of cattle food depends on the relative prices of sugar and molasses at the time.

It is stated in the literature, that cane-sugar molasses

cannot be treated by the Steffen process owing to the presence in it of a considerable quantity of invert sugar which would be decomposed by lime giving dark-coloured and troublesome decomposition products. One suggestion for the recovery of sucrose from cane-sugar molasses is to ferment it by a special yeast that acts on the invert sugar only, then to distil off the alcohol and recover sucrose from the spent wash by Steffen's process. Apparently there are yeasts which under carefully controlled conditions will ferment invert sugar and leave sucrose unattacked but it has not yet been possible to operate with these yeasts on a manufacturing scale.

Battelle's process (*J. Soc. Chem. Ind.*, 1912, *31*, 1195; 1915, *34*, 916; 1919, *38*, 784A) for manufacturing sugar from sugar-cane contains the essentials of a method for recovering sucrose from cane sugar molasses. In this process the juice is heavily limed and subjected to a vigorous boil which decomposes invert sugar in the juice with production of colourless or light coloured substances instead of those dark-coloured products obtained by the action of lime at lower temperatures. The juice is then carbonated, etc., as in the ordinary process for manufacturing sugar and the molasses left, after the sugar has crystallised, is like beet-sugar molasses in character (since it contains no appreciable quantity of invert sugar) and is treated by Steffen's process.

Battelle's process has been given a trial on a large scale. Undoubtedly it gives a larger yield of sugar from the juice but the increase of yield has not been considered sufficient to justify the additional plant and treatment necessary.

With slight modification the process would seem to be suitable for the recovery of sucrose from cane-sugar molasses as a process by itself, viz., by diluting the molasses and boiling with lime to destroy the invert

sugar, then precipitating the sucrose as tricalcium sucrate filtering and treating with carbonic acid to liberate sucrose. The present investigation is an examination of this process.

PRELIMINARY EXPERIMENTS

(PERFORMED BY THE LATE D. N. GUPTA.)

Precipitation of Sucrose by Lime.

It appears that it is necessary to use freshly burnt lime in a finely ground condition and to stir this gradually into the cooled sucrose solution in order to get a good precipitation of the sucrate.

After trying several experiments it was found that the best precipitation of sucrose could be obtained by taking a 12 per cent. solution of sucrose and gradually stirring in a quantity of lime equal to the weight of sucrose taken, the stirring being mechanically continued for 4 hours at a temperature of 0—6°. The precipitate was collected and the filtrate was boiled and filtered until no more precipitate appeared. Sucrose was estimated in the final filtrate by the polarimeter.

(a). Temperature 0-6°; 30 g. sucrose, water and lime in proportion, 5·8 g. sucrose left in filtrate; 80·6 per cent. sucrose precipitated.

(b). Another 15 g. lime were stirred into the final filtrate of above, mixture filtered, etc., 4·8 g. sucrose left in filtrate; total sucrose precipitated = 84 per cent.

Longer stirring did not improve matters and higher working temperatures gave low yields.

Destruction of Glucose by Boiling with Lime.

Several experiments were tried by boiling a mixture of sucrose and glucose in aqueous solution with lime

varying the quantity of lime aud the duration of boiling. It was found that boiling the solution for 2 hours with a quantity of lime equal to the quantity of glucose in solution was sufficient to destroy the glucose almost completely, glucose left undestroyed in the solution after boiling with lime was estimated by Fehling's solution, the precipitate of cuprous oxide being collected and estimated by the volumetric permanganate method (Browne, "Hand book of Sugar Analysis," p. 410).

Twelve g. sucrose, 4 g. glucose, 3 g. lime, 100 c. c. water, boiled for 2 hours; 0·217 g. glucose left.

There is no appreciable destruction of sucrose by this treatment.

Recovery of Sucrose from a Mixture of Sucrose and Glucose.

Eight g. sucrose and 4 g. glucose were dissolved in 160 c. c. water (making a solution containing approximately the same quantities of sucrose and glucose as in molasses diluted to 12° Brix) and boiled with 3 g. lime for 2 hours. Then in the course of 3 hours 9 g. freshly burnt finely ground lime were gradually stirred in to the mixture at a temperature of 0°—10°. The solid was collected, the filtrate boiled etc., as in the experiments on the precipitation of sucrose. Sucrose in filtrate=0·718 g. (8·9 per cent. of sucrose taken); glucose in filtrate= 0 025 g.

The cake was suspended in water and decomposed by carbonic acid.

Sucrose recovered from cake by 2½ hours' carbonation

=4·68 g.

Sucrose recovered by an extra 2 hours' carbonation

=1·52 g.

Total sucrose recovered from cake   =6·20 g.

This is a recovery of 77·5 per cent. of sucrose in original mixture.

Recovery of Sucrose from Molasses.

Twenty g. molasses (containing 43 per cent. sucrose and about 20 per cent. glucose) were dissolved in 100 c. c. water and treated by the same process.

(a) Sucrose in filtrate = 2·64 g. (30·7 per cent. of sucrose in molasses).

    Glucose   ,,   = 0·028 g.

(b) Sucrose in filtrate = 2·22 g. (25·8 per cent. of sucrose in molasses).

    Glucose   ,,   =0·018 g.

(c) Sucrose in filtrate = 1·8 g. (20·9 per cent. of sucrose in molasses).

In the last experiment the cake was carbonated.

Sucrose recovered from cake = 5·7 g. (66·3 per cent. of sucrose in molasses).

The sucrose recovered was by no means colourless. The purity was calculated from the density of the sucrose solution and found to be 66 per cent.

Recovery of Sucrose from a Mixture of Sucrose and Glucose (repeated).

The low purity of the sucrose recovered from the molasses made it desirable to go back and repeat the experiment with a mixture of sucrose and glucose and determine the purity of the sucrose isolated. This had not been done in the previous experiment. The only modification was that the mixture was boiled with the lime for 4 instead of 2 hours.

Sucrose recovered from cake = 5·38 g. (67·2 per cent. of sucrose taken).

Glucose in product recovered from cake = 0·15 g.

Purity of recovered sucrose = 60·8 per cent.

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Treatment of Glucose only by same Process.

If seemed possible that the low purity of the sucrose obtained by carbonating the cake might be due to the precipitation as insoluble lime compounds of the decompostion products from the glucose. To ascertain whether this was the case 4 g. of glucose only were put through the same process, but on carbonating the cake only 0·358 g. solid was obtained which is an insignificant quantity compared with the 3·5 g. of other solids which were mixed with the recovered sucrose in the last experiment.

Attempt to Recover Sucrose of Higher Purity from a Mixture of Sucrose and Glucose.

(a) *By washing the cake with hot water.*

The last experiment indicated that the impurities in the recovered sucrose were due to impurities retained mechanically or by adsorption in the lime sucrate cake. An attempt was made to remove these impurities by boiling the cake with 100 c. c. water and again filtering.

Sucrose recovered from washed cake = 0·39 g.
Sucrose in wash-water   = 3·85 g.

This unexpected result showed that washing the cake, even with hot water, lowered the yield of sucrose to an extent to make the process technically useless. The result was unexpected because the solubility of tricalcium sucrate is recorded in the literature as 1 part in 200 parts boiling water and 1 part in 100 parts cold water so that not more than 0·5 g. tricalcium sucrate equivalent to about 0·33 g. sucrose was expected to be dissolved by the wash-water.

(b) *By carbonating the mixture after the lime-boil and before precipitation of the lime sucrate.*

Just as juice is purified by the carbonation process it was thought possible to remove the impurities by

carbonating after the lime-boil, filtering and rejecting the calcium carbonate, then cooling the filtrate, stirring in the rest of the lime to precipitate the lime sucrate, and proceeding as before.

(1) Sucrose recovered from cake = 4·68 g. (58·5 per cent. of sucrose taken).

Purity of recovered sucrose = 84·6 per cent.

(2) The carbonation, after the lime-boil, was carried out in two stages as in the factory process. The cake was also carbonated in two stages. The colour of the recovered sucrose was considerably improved.

Sucrose recovered from cake
by first carbonation = 2·15 g. (purity 83 per cent.)

Sucrose recovered from cake
by second carbonation = 2·91 g. (purity 98 per cent.)

Total sucrose recovered = 5·06 g. (63·2 per cent. of sucrose taken.)

It appears that with some sacrifice in yield the purity of the recovered sucrose can be considerably raised by carbonation after the lime-boil.

Attempt to Recover Sucrose of higher Purity from Molasses by Carbonating the Mixture after the Lime-boil and before Precipitation of the Lime Sucrate.

Twenty g. of molasses were treated.

(a) Sucrose recovered from cake = 3·95 g. (45·9 per cent. of sucrose in molasses).

Purity of recovered sucrose
(calculated from density of
sucrose solution)* = 60·2 per cent.

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* Purity calculated from weight of total solids on evaporating sucrose solution.

Purity of recovered sucrose (cal-
culated from weight of total
solids left on evaporating
sucrose solution) $= 69 \cdot 9$ per cent.

Sucrose recovered from cake in two stages.

Sucrose recovered from first
carbonation   ...   ... $= 3 \cdot 95$ g.   (purity
                                            $78 \cdot 7$ per cent). .

Sucrose recovered from second
carbonation   ...   ... $= 0 \cdot 26$ g.

_____

Total sucrose recovered $= 4 \cdot 21$ g. (49 per
cent. of sucrose in molasses).

This result with molasses is disappointing in compari-
son with that obtained with a mixture of sucrose and glu-
cose both as regards yield and purity.

Calculation shows that unless a better yield and
better purity can be obtained the process is commercially
useless. Taking molasses at Rs. 2, sugar at Rs. 12, and
quicklime at 12 as. per maund, and reckoning on a yield of
crystalline sugar equal to 50 per cent. of the sugar in the
molasses, we have

Cost of 100 md. molasses ...   ... Rs. 200
Cost of 60 md. lime   ...   ... ,,   45

_____

                                         Rs. 245

Value of 20 md. sugar produced ... Rs. 240

EXPERIMENTS TO INCREASE THE YIELD OF SUCROSES

(PERFORMED BY H. S. CHATURVEDI).

In the preliminary experiments the best precipitation
of sucrose was 84 per cent., the best recovery of sucrose
77 per cent. whilst with molasses it was not much more
than 50 per cent. Attempts were made to improve the
precipitation.

Precipitation of Sucrose by Lime.

In repeating Mr. Gupta's experiments with pure sucrose solution the precipitation of sucrose was not so good as obtained by Mr. Gupta, the precipitation being about 60 per cent.

Attempts were made to improve the precipitation by using (a) freshly prepared cream of lime, (b) freshly burnt quick-lime which had been passed through a 100-mesh sieve but the results were still worse, precipitation being 38·5 per cent., and 41·5 per cent., respectively. Arguing that the insoluble lime sucrate might produce a coating round the particles of lime and prevent further action it was decided to stir in the lime in two instalments, filtering before the second addition. This gave very good results.

(1) Temperature 0°—5°; 12 g. sucrose in 100 c. c. water; 12 g. lime in 2 instalments; 0·61 g. sucrose left in solution; 95 per cent. sucrose precipitated.

(2) Temperature 0°—5°; 12 g. sucrose in 100 c. c. water; 12 g. lime in 2 instalments; 0·61 g. sucrose left in solution; 97·8 per cent. sucrose precipitated

Recovery of Sucrose from Molasses by Adding Lime in two Instalments.

Twenty g. of molasses were dissolved in 115 c.c. water, boiled with 3 g. lime for two hours and then cooled to 0—5° and 9 g. lime added in two instalments.

(*a*). Sucrose in filtrate = 0·92 g.; 93 per cent. sucrose precipitated.

(*b*). Sucrose in filtrate = nil; 100 per cent. sucrose precipitated... Sucrose recovered from cake = 7·18 g. (83·7 per cent. of sucrose in molasses).

Purity of recovered sucrose
(total solids by weighing) = 70·5 per cent.
,, (total solids by density of sucrose solution) = 65·6 per cent.

Recovery of Sucrose from Molasses, Carbonating after the Lime-boil and Precipitating Lime Sucrate by Adding Lime in two Instalments.

Twenty g. of molasses treated.

(*a*). Sucrose in filtrate $= 0 \cdot 88$ g. ($10 \cdot 2$ per cent. of sucrose in molasses).

Sucrose recovered from cake $= 5 \cdot 9$ g. ($68 \cdot 6$ per cent. of sucrose in molasses).

Purity (total solids by weighing) $= 77$ per cent.

(total solids by density of sucrose solution) $= 70 \cdot 6$ per cent.

(*b*). Sucrose in filtrate $= 1 \cdot 3$ g. ($15 \cdot 1$ per cent. of sucrose in molasses).

Sucrose recovered from cake $= 4 \cdot 68$ g. ($54 \cdot 4$ per cent. of sucrose in molasses).

Purity (by weighing total solids) $= 70 \cdot 9$ per cent.

The addition of lime in two instalments considerbly increases the yield of sucrose but the process cannot be considered satisfactory because the purity of the recovered sucrose is low. It is remarkable that so large an amount of impurity is retained, mechanically or by adsorption by the lime sucrate; in the case where the sucrose recovered from the cake was $7 \cdot 18$ g. and the purity $70 \cdot 5$ per cent., about 3 g. of impurities were present in the precipitate.

EXPERIMENTS TO IMPROVE THE PURITY OF THE RECOVERED SUCROSE

(PERFORMED BY P. S. CHATURVEDI).

In order to be sure that the low purity of the recovered sucrose is not due to the formation of an insoluble lime compound of the decomposition products of the glucose

the experiment was repeated in which glucose only was put through the process. From 4 g. of glucose only 0·36 g. total solids was recovered on carbonating the cake, confirming the previous experiment.

Purity of Sucrose Recovered from a Mixture of Sucrose and Sodium Chloride.

Sodium chloride was chosen as a simple crystalloid which would have little tendency to be adsorbed.

Eight g. of sucrose and 4 g. sodium chloride were dissolved in 100 c. c. water and treated with 12 g. lime in two instalments, precipitate being washed as in previous experiments.

- Sucrose in filtrate = 2·34 g.
  Sucrose recovered from cake = 1·94 g.
  Purity of recovered sucrose (total
    solids by weighing) = 85·9 per cent.
  Purity of recovered sucrose (total
    solids by density of sucrose
    solution) = 77·9 per cent.

This experiment shows that even a simple salt like ommon salt is retained by the precipitate to a consider-ble extent.

Recovery of Sucrose from a Mixture of Sucrose and Glucose. Washing the Lime Sucrate Cake with Rectified Spirit.

Precipitate washed in original funnel with 100 c. c. cold rectified spirit.

Sucrose in original filtrate = 1·14 g.
Sucrose recovered from cake = 5·33 g.
Purity (by weighing total solids) = 81·6 per cent.
Sucrose recovered from cake by
  second carbonation = 0·26 g.

There is an improvement in purity but nothing considerable.

Recovery of Sucrose from a Mixture of Sucrose and Glucose, Washing the Lime Sucrate with boiling Water and Reprecipitating the Sucrose from the Wash-water.

In inorganic analysis a precipitate which is impure on account of adsorption is purified by re-dissolving and re-precipitating. It was decided to apply this process to the lime sucrate. The cake obtained in the usual way was mixed with 100 c. c. boiling water in a mortar and filtered; residue = ppt. (A).

The filtrate was boiled and filtered; residue = ppt. (B). The filtrate was cooled to 0-6° and 4·5 g. lime stirred in.

The solid was collected = ppt. (C). The filtrate is called the second filtrate.

PURITY.

	I		II	
Sucrose in 1st filtrate,	0·70 g.		6·67 g.	
,, ppt. (A)	1·09	82·2 p. c.	2·00	78·6 p. c.
,, ppt. (B)	2·00	82·7 p. c.	0·65	75·8 p. c.
,, ppt. (C)	1·04	86·1 p. c.	1·40	84·1 p. c.
,, 2nd filtrate,	0 65		0·88	
Sucrose in total carbonated cake = 2·60 g.				
Total sucrose accounted for	**5·48**		**8·20**	

	III		IV	
Sucrose in 1st filtrate,	0·26 g.		1·10 g.	
,, ppt. (A)	2·18	80·5 p.c.	2·96	79·5 p.c.
,, ppt. (B)	1·56	78·6 p.c.	0·88	81·5 p.c.
,, ppt. (C)	1·35	86·0 p.c.	0·52	91·2 p.c.
,, 2nd filtrate,	1·20		0·67	
,, Total carbonated cake,	0·90		0·20	
Total sucrose accounted for	**7·45**		**6·33**	

In the first experiment there was a large proportion of sucrose unaccounted for. The second experiment indicated that this had been due to incomplete decomposition of the lime sucrate by carbonic acid. In the second and third experiments the lime sucrate was mixed with water and boiled whilst carbon dioxide was passed in. This made the decomposition of the lime sucrate more complete.

Recovery of Sucrose from Molasses, Washing the Lime Sucrate with boiling Water and Reprecipitating the Sucrose from the Wash-water.

Twenty g. of molasses were treated as above.

Sucrose in 1st filtrate	...	...	0·88 g.
,, in ppt. (A)	...	...	3·74 (purity, 73·7 p. c.)
,, in ppt. (B)	...	...	0·10 (,, 66·4 p. c.)
,, in ppt. (C)	...	...	1·23 (,, 80·6 p. c.)
,, 2nd filtrate	...	...	1·14
,, total carbonated cake	...	...	0·23
Total sucrose accounted for			7·32 g.

An increase of purity has been attained with considerable loss of yield. A yield of 59 per cent. sucrose with average purity of 75 per cent. is to be compared with 83·7 per cent. yield of purity 70·5 per cent. (without treatment of the cake). Obviously the increase in purity does not counterbalance the loss in yield.

Experiments to destroy the Glucose by other Methods with a View to Improve the Purity of the Recovered Sucrose.

It was thought that if the glucose was destroyed by caustic soda or by lime at lower temperature, the decomposition products, being different from those formed

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by lime at the boil, might not be retained to the same extent by the lime sucrate.

Decomposition of Glucose by boiling with Caustic Soda Solution.

(a) Eight g. sucrose, 4 g. glucose, 0·8 g. caustic soda dissolved in 100 c.c. water and boiled for 1 hour; at the end of this time the solution was no longer alkaline; glucose left in solution = 1·92 g.

(b) Eight g. sucrose, 4 g. glucose, 1·5 g. caustic soda dissolved in 100 c.c. water, and boiled for 2 hours; the solution was alkaline and contained 0·49 g. glucose.

(c) Eight g. sucrose, 4 g. glucose, 1·5 g. caustic soda dissolved in 100 c.c. water, and boiled for 3 hours; 0·38 g. glucose left in solution.

Recovery of Sucrose from a Mixture of Sucrose and Glucose, Decomposing the Glucose by boiling with Caustic Soda.

The experiment was carried out as in (b) above, then the mixture was cooled to $0-6°$, and 9 g. lime in two instalments were stirred in.

Sucrose in filtrate = 0·57 g.

Sucrose recovered from cake = 4·94 g.

Purity (total solids by weighing) = 80·1 per cent.

This result is not strikingly better than those obtained with lime.

Decomposition of Glucose by Lime at lower Temperatures.

(a) Eight g. sucrose, 4 g. glucose, 3 g. lime and 8 c.c. water were allowed to stand at the ordinary temperature for 42 hours; glucose left = 2·47 g.

(b) Eight g. sucorse, 4 g. glucose, 3 g. lime and 8 c.c. water were allowed to stand at the ordinary temperature

at 70° for 2 hours; glucose left=0·28 g.; colour of solution very dark.

(c) Eight g. sucrose, 4 g. glucose, 3 g. lime and 8 c.c. water were allowed to stand at the ordinary temperature at 70° for 4 hours; glucose left = 0·20 g.; colour of solution very dark.

This is not a promising way of decomposing the glucose owing to the dark colour of the decomposition products.

Conclusion.

The results so far obtained have been collected together for publication, although it is obvious that success has not yet been attained in the solution of the problem. A striking feature of the results is their irregularity. The same experiment repeated never gives quite the same results and often the variation is considerable.

Perhaps the most puzzling feature is the solubility of the lime sucrate in boiling water, which is much greater than that recorded in the literature. The experiments on washing the lime sucrate with hot water gave most variable results. It seems as though the lime sucrate precipitated in the cold is not true tricalcium sucrate; and perhaps if the conditions could be found for a fairly complete precipitation of the true tricalcium sucrate the problem would be solved. The lime sucrate formed is gelatinous and therefore difficult to wash. If it could be obtained crystalline or at any rate not gelatinous it could probably be washed more easily.

But the results so far obtained are quite promising from the commercial standpoint. By the simplest process we have obtained a recovery of 84 per cent. of the sugar in molasses in the form of a syrup of 70 per cent. purity. If we assume that this syrup, on boiling, would give crystalline sugar and leave molasses of 40 per cent. purity

we could get 24 parts of crystalline sugar and 24 parts of molasses from 100 parts of molasses containing 40 per cent. sucrose. Taking the same prices for molasses and sugar as in our previous calculation we have—

100 md. of molasses	...	Rs. 200
60 md. of lime ...	...	„ 45
	Total	Rs. 245

Value of 24 md. sugar produced @ Rs. 12 per md. Rs. 288
Value of 24 md. molasses produced ... „ 48

	Total	Rs. 336

This leaves a considerable margin for working charges.

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Studies in Ring Formation.

By

ANUKUL CHANDRA SIRCAR AND PRAN KUMAR DE.

The investigation may conveniently be divided into three parts, A, B and C.

A. *Attempts to prepare* p-*Diphenylene.*

For substances like benzidine or naphthalene Kaufler (*Annalen*, 1907, *351*, 151) proposed a theory according to which the two phenyl groups in the molecule of benzidine do not lie on one plane—the valency joining them being not fixed in space, but in an oscillatory condition.

(I)
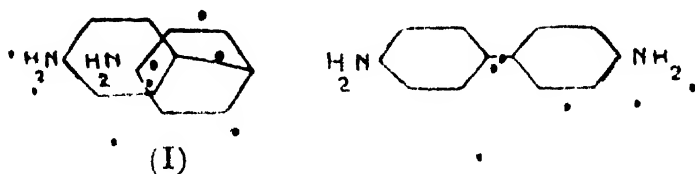
Hence the two amino groups are sometimes near one another, as shown in (I), and should together have the effect of an *ortho*-diamine. According to this conception diphenyl becomes a derivative of a hypothetical substance, namely, p-diphenylene:—

$$\begin{array}{ccc} C_6H_4 & & C_6H_5 \\ | \ | & \longrightarrow & | \\ C_6H_4 & & C_6H_5 \end{array}$$
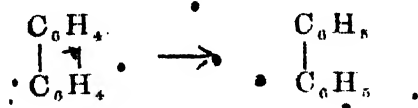
This substance is unknown. Dobbie, Fox and Gauge (*J. Chem. Soc.*, 1911, *99*, 683) have prepared *o*-diphenylene.

It is obvious that Kaufler's conception of diphenyl would be supported if the parent hydrocarbon, namely *p*-diphenylene were obtained. From a study of the literature of the subject, it appears that no attempt had been made in a plausible direction for the preparation of *p*-diphenylene.

·Ullmann (*Annalen*, 1904, *332*, 38) and others have shown that iodo-compounds are better adapted than chloro- or bromo-compounds for the preparation of polycyclic substances from mono-cyclic ones and that finely divided copper is suitable for the elimination of halogen atoms. The authors thought that if benzidine has the "butterfly" constitution suggested by Kaufler, then $p : p'$-di-iodo-diphenyl must be similar, and that on treatment with copper powder might yield *p*-diphenylene.

$$IC_6H_4 \cdot C_6H_4I + 2Cu \quad = \quad \begin{array}{c} C_6H_4 \\ | \quad | \\ C_6H_4 \end{array} + Cu_2I_2$$
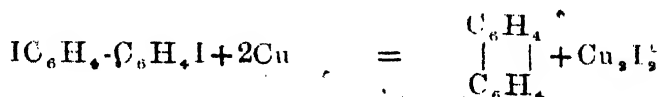
Repeated attempts to eliminate the iodine atoms in $p : p'$-di-iodo-diphenyl were unsuccessful.

p-Di-iodobenzene was next tried, the iodine atoms in that substance also being favourably situated for the formation of *p*-diphenylene,

$$2C_6H_4I_2 + 4Cu \quad \longrightarrow \quad \begin{array}{c} C_6H_4 \\ | \quad | \\ C_6H_4 \end{array} + 2Cu_2I_2$$
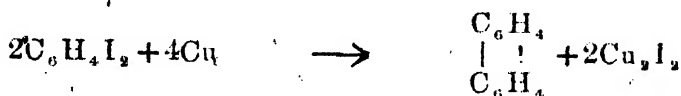
The results obtained were as disappointing as before. In one experiment a small amount of a white crystalline substance was isolated. But on examination it was found to be only $p : p'$-di-iodo-diphenyl, so that only one of the iodine atoms was eliminated from each molecule.

Thus attempts to prepare *p*-diphenylene have so far been unsuccessful.

B. *Attempts to prepare Derivatives of* p:p'-*Diazo-phenylene.*

Kaufler (*loc. cit.*) has said that various other types of *p* : *p'*-diamino compounds *viz*, *p* : *p'*-diamino-diphenyl methane and *p* : *p'*-diamino-stilbene behave in the same way as benzidine, *i.e.*, show the properties of an *ortho*-diamine. From the similarity in the constitution of *p* : *p'*-diamino-stilbene and of *p* : *p'*-diamino-azo-benzene there seemed to be no reason why the latter substance should not also behave like an *ortho*-diamine. The present part of the investigation is concerned with that problem and with attempts to prepare derivatives of *p* : *p'*-diazophenylene: The problem was attacked in the same way as was followed in the case of benzidine by Kaufler (*loc. cit.*), Cain and Micklethwaite (*J. Chem. Soc.*, 1914, *105*, 1437) and Turner and his colleagues (*J. Chem. Soc.*, 1915, *107*, 1495; 1917, *111*, 1; 1920, *117*, 1140).

Bandrowski (*Ber.*, 1884, *17*, 1181) prepared diphthalyl benzidine. Gustav Koller (*Ber.*, 1904, *37*, 2880), by the actions of phthalic anhydride on benzidine, prepared a phthalyl derivative which was found to be different from Bandrowski's compound. Kaufler, by a determination of the molecular weight of Koller's phthalyl derivative as well as of the compound obtained by the action of oxalyl chloride on benzidine, proved that in either case they were formed by the condensation of one molecule of each of the reacting substances, and brought forward this as an argument in favour of the *o*-diamine

formula of benzidine. Another proof of the advantages of Kaufler's formula was brought forward by Cain and Micklethwaite, who found that o-diketones, like benzil and glyoxal, condense with benzidine to give compounds of the type,

$$\begin{array}{c} C_6H_4-N=CR \\ | \qquad | \\ C_6H_4-N=CR \end{array}$$
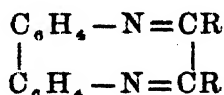
However, attempt to repeat Cain and Micklethwaite's works made by Ferriss and Turner (*J, Chem. Soc.*, 1920, *117*, 1140) and by the authors were unsuccessful.

Turner (*J. Chem. Soc.*, 1915. *107*, 1496) tried the reaction of acetylacetone on benzidine in the expectation that if benzidine possesses an *ortho*-diamine formula the two ketonic groups of acetylacetone will condense with one molecule of benzidine to yield a compound of the type

$$\begin{array}{c} C_6H_4-N=C< \begin{array}{c} R \\ CH_2 \end{array} \\ | \\ C_6H_4-N=C< \begin{array}{c} \\ R \end{array} \end{array}$$
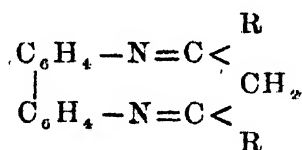
The results obtained were, however, quite different from those expected.

It has now been found that phthalic anhydride does not react with $p . p'$-diamino-azo-benzene; phthalyl chloride reacts with it to form a diphthalyl derivative *i.e.*, two molecules of phthalyl chloride react with one molecule of $p : p'$-diamino-azo-benzene. Owing to the extreme insolubility in all organic solvents of the condensation product of oxalyl chloride and $p : p'$-diamino-azo-benzene, it could not be decided whether it was formed by the condensation of one molecule of oxalyl chloride with one molecule of $p : p'$-diamino-azo-benzene or by the condensation of two molecules of each of the two substances.

Glyoxal or benzil could not be made to react with $p : p'$-diamino-azo-benzene. Acetylacetone reacts with the

diamino-compound in the same way as it does with benzidine (Turner, *loc. cit.*) and an azo-quinoline derivative is formed.

$$N.C_6H_4.NH_2 \atop N.C_6H_4.NH_2 \quad + \quad 2\ CH_3.CO.CH_2.CO.CH_3$$

$$\rightarrow \quad N.C_6H_4.N=C(CH_3).CH_2.CO.CH_3 \atop N.C_6H_4.N=C(CH_3).CH_2.CO.CH_3$$

$\rightarrow$
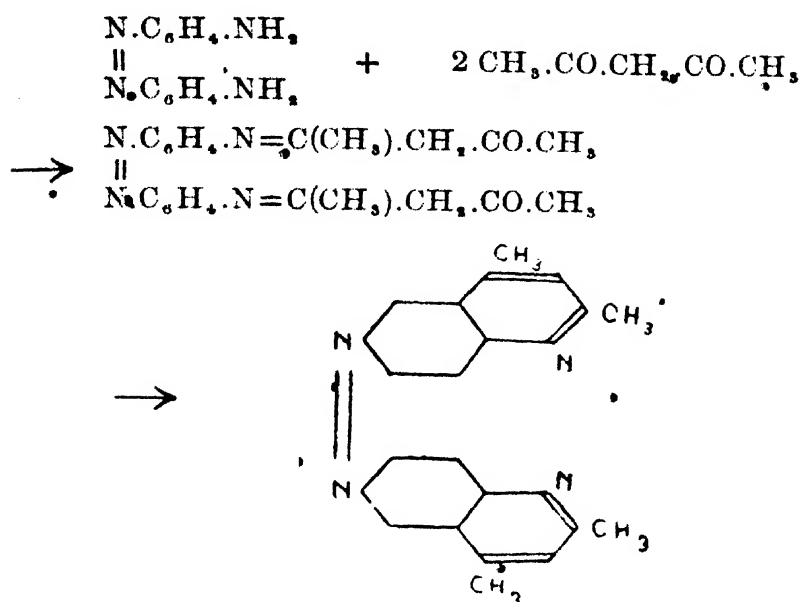
Thus attempts to prepare derivatives of $p : p'$-diazophenylene have also been so far unsuccessful.

C. *Action of Aldehydes on Benzidine and* p : p'-*Diaminoazo-benzene.*

A characteristic reaction of the *ortho*-diamine is the readiness with which they condense with aldehydes to form iminazolones. The action of anisaldehyde on benzidine and that of salicylaldehyde and of resorcylaldehyde on $p : p'$-diamino-azo-benzene has now been tried. In every case two molecules of the aldehyde are found to react with one molecule of the diamino compound and it was found that there was not the slightest tendency towards iminazolone formation.

Conclusion.

The results obtained so far all go against Kaufler's formula for benzidine and similar $p : p'$-diamino-substances.

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EXPERIMENTAL.

An intimate mixture of *p*-di-iodobenzene (9·30 g.) and finely divided copper powder (Natur Kupfer C, 17·5 g.) was heated at 300—330° for three hours, after which time the copper was found to have lost its lustre. The contents of the tube were taken out and weighed; separate portions were treated respectively with acetic acid, ether, alcohol, chloroform, benzene and nitrobenzene. It was found that nothing was extracted by organic solvents.

A portion of the product was boiled with concentrated hydrochloric acid for five minutes and the mixture was filtered. On making the filtrate alkaline a reddish looking heavy precipitate was obtained in good yield. On examination it was found to contain copper and was therefore not further examined.

The above experiment was repeated several times at different temperatures, but with no better result.

2:4:2':4'-*Tetramethyl-azo-quinoline.*

4:4'-Diamino-azo-benzene (0·55 g.) was warmed with acetylacetone (1·5 g.) until everything went into solution. The solution was then boiled for two minutes more. On cooling a crystalline solid separated. This was collected and recrystallised from alcohol as shining red prisms (m. p. 192—193°). It is soluble in alcohol and acetic acid, insoluble in water and dilute hydrochloric acid. (Found: N = 16·12, 15·86. $C_{22}H_{20}N_4$ requires N = 16·47 per cent.).

Diphthalyl benzidine was obtained as shining yellow needles on adding phthalyl chloride (2 g.) to a solution of benzidine (1 g.) in nitrobenzene (40 c. c.). On examination it was found to be identical with the compound obtained by Bandrowski (*loc. cit.*).

Diphthalyl-4:4′-diamino-azo-benzene.

$$C_6H_4 < ^{CO}_{CO} > N \cdot C_6H_4 \cdot N = N \cdot C_6H_4 \cdot N < ^{CO}_{CO} > C_6H_4$$
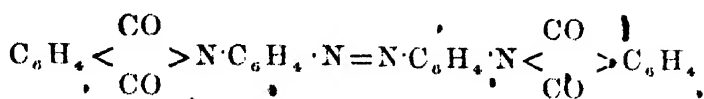
A solution of 4:4′-diamino-azo-benzene (1 g.) in the least quantity of nitrobenzene was treated with phthalyl chloride (2 g.) when at once a black precipitate appeared. It was boiled for half an hour when the colour changed from black to brown. The solid was then filtered, washed with ether and crystallised from nitrobenzene: light-brown needles, m. p. above 300°.

It is insoluble in ether, acetic acid and alcohol. (Found: $N = 12 \cdot 32$. $C_{28}H_{16}N_4O_4$ requires $N = 11 \cdot 85$ per cent.).

Oxalyl-4:4′-diamino-azo-benzene.

$$\begin{array}{l} CO-NH-C_6H_4-N \\ | \qquad\qquad\qquad \| \\ CO-NH-C_6H_4-N \end{array} \quad or \quad \begin{array}{l} CO-NH-C_6H_4 \cdot N=N \cdot C_6H_4-NH-CO \\ | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ CO-NH-C_6H_4 \cdot N=N \cdot C_6H_4-NH-CO \end{array}$$
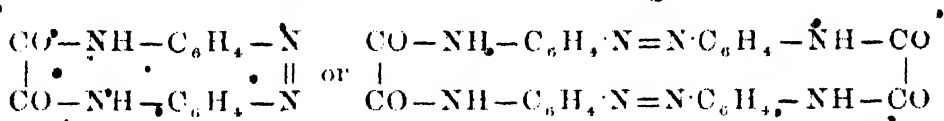
A solution of 4:4′-diamino-azo-benzene (1 g.) in cold nitrobenzene (80 c.c.) was treated with oxalyl chloride (2 c.c.) when at once a reddish precipitate appeared. The solution was then boiled for half an hour and the colour of the precipitate changed to light yellow. It was purified by boiling successively with nitrobenzene and pyridine and filtering hot when the substance remained on the filter paper as light yellow particles, m. p. above 300°. It is insoluble in organic liquids. (Found: $N = 20 \cdot 93$. $C_{14}H_{10}O_2N_4$ requires $N = 21 \cdot 05$ per cent.).

Benzidine-bis-(p-methoxy-phenyl-azo-methine).

$$CH_3O \cdot C_6H_4 \cdot CH = N \cdot -C_6H_4 \cdot -C_6H_4 \cdot N = CH \cdot C_6H_4 \cdot OCH_3$$
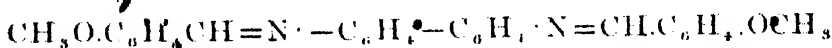
Benzidine (1 g.) was dissolved in alcohol (60 c.c.) and the solution was cooled to 0°. It was then treated with anisaldehyde (0·73 g.) and a light yellow precipitate appeared gradually. After half an hour the mixture was

filtered. The solid product was crystallised from nitrobenzene : shining light yellow plates, m. p. 246-48°.

It is very slightly soluble in alcohol, more so in acetic acid and nitrobenzene. It is readily hydrolysed to benzidine and the aldehyde on warming with dilute hydrochloric acid. (Found : N $= 7.09$. $C_{28}H_{24}N_2O_2$ requires N $= 6.67$ per cent.)

Azo-benzene-p ɩ p'-bis-(hydroxy-phenyl-azo-methine).

$$OH.C_6H_4.CH=N \cdot C_6H_4 \cdot N=N \cdot C_6H_4 \cdot N=CHC_6H_4.OH$$
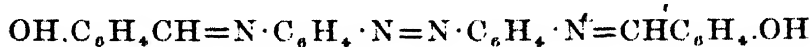
A cold solution of 4 : 4'-diamino-azo-benzene (0·5 g.) in alcohol (60 c.c.) was treated with salicylaldehyde (0·5 g.) when at once a reddish crystalline precipitate appeared. It was filtered and recrystallised from nitrobenzene :, light brown shining plates, m. p. 265°.

It is insoluble in alkali, dilute hydrochloric acid and in alcohol, soluble in warm acetic acid and nitrobenzene. (Found : N $= 13.36$. $C_{26}H_{20}N_4O_2$ requires N $= 13.33$ per cent.).

Azo-benzene-p : p'-bis-(3 : 4-dihydroxy-phenyl-azo methine).

$$(OH)_2C_6H_3.CH=N \cdot C_6H_4 \cdot N=N \cdot C_6H_4 \cdot N=CH.C_6H_3(OH)_2$$
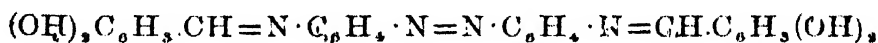
A solution of 4 : 4'-diamino-azo-benzene (0·5 g.) in hot alcohol (60 c.c.) was treated with resorcylaldehyde (0·5 g.). After boiling for half an hour the solution, was allowed to cool when a reddish-brown crystalline precipitate gradually separated. This was filtered, washed with warm alcohol and dried. It begins to darken at about 250° but does not melt below 270°. It is readily hydrolysed by cold alkali. It is slightly soluble in alcohol, readily soluble in acetic acid. (Found : N $= 12.62$. $C_{26}H_{20}N_4O_4$ requires N $= 12.39$ per cent.).

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The Preparation of Camphor from Pinene.

BY

H. M. MULANY AND E. R. WATSON.

The preparation of camphor from French and American turpentine, the chief constituent of which is pinene, is already a commercial proposition. Nevertheless the details available in the scientific literature are meagre. We found that research was necessary before we could obtain a satisfactory yield of camphor from pinene. The results are published with a view to supplement the information available in the literature.

As our work was instigated by a desire to prepare camphor from Indian turpentine, which does not give any appreciable yield of pinene hydrochloride, we selected those methods which do not require the intermediate production of pinene hydrochloride. The process which has been worked successfully is as follows:—

Pinene —> Bornyl salicylate —> Borneol —> Camphor.
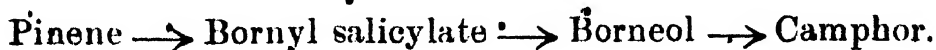
Bornyl salicylate was prepared according to Chemische Fabrik von Heyden (D.R.P. 175097, *J. Chem. Soc.*, 1907, 92, i, 429). Two parts of salicylic acid and 1 part of pinene distilled from French turpentine were heated together for 17 hours at 110° and gradually raised to 150° in 11 hours. The product was shaken with aqueous sodium carbonate to remove unchanged salicylic acid,

extracted by ether, dried, freed from ether and distilled *in vacuo.* It gave 70·8 per cent. (reckoned on the weight of pinene) of bornyl salicylate distilling at 178—182°/7 mm. A large fraction distilled at 60—80°/7 mm., and could perhaps be utilised for the preparation of a further quantity of bornyl salicylate.

On using equal parts of salicylic acid and pinene (molecular proportions) the yield was 59 per cent of bornyl salicylate.'

Borneol was obtained by boiling 1 part of bornyl salicylate with 5 parts of 20 per cent. alcoholic potash under the reflux for 8—10 hours. The product was poured into water and steam distilled. The semi-solid which separated from the distillate was collected and pressed between blotting paper; the yield was 44 per cent. of the theoretical of fairly pure borneol. The oil which was removed from the solid during the filtration was re-saponified but did not give any appreciable yield of borneol. Saponification with aqueous and alcoholic potash under various conditions did not give any better yield.

Camphor was prepared from the borneol by shaking with 5 parts of 50 per cent. nitric acid (containing a trace of nitrous acid) for 3 hours in a shaking machine. The mixture was diluted with water and the camphor filtered off. Yield 50 per cent.

Attempts to obtain a better yield of camphor by directly oxidising bornyl salicylate, and attempts to use sodium peroxide as an oxidising agent, as described in the literature, were not successful.

A Note on the Bleaching of Shellac.

BY

E. R. Watson and H. M. Mulany.

The bleaching of shellac, as described in Rogers and Aubert's "Industrial Chemistry," 1912, p. 701, is effected by sodium hypochlorite in a hot alkaline solution of the shellac. In the same place it is stated that a peculiarity of bleached shellac is its gradual change into a modification insoluble in alcohol and alkalis, which change inevitably takes place in time with every bleached shellac. The change is said to be favoured by high temperatures.

Gadre describes the bleaching of shellac (*Chem. News*, 1921, *123*, 127), the process being essentially the same as described by Rogers and Aubert. He gives figures showing that a sample which was almost completely soluble in alcohol when freshly made was soluble only to the extent of 56·6 per cent. after exposure to light and air for 6 months. Also he analysed an old sample of English make and found it was soluble only to the extent of 12·1 per cent.

Rogers and Aubert prescribe the preparation of a solution of sodium hypochlorite, (from 10 kg. bleaching powder for every 10 kg. shellac) and direct that it should be added to the hot alkaline solution of the shellac until the latter becomes wine-yellow in colour. They

do not state how much of this solution is' generally required. Gadre used the whole of the hypochlorite solution obtained from 1 part of bleaching powder for the bleaching of 1 part of shellac.

The present authors have bleached shellac by Rogers and Aubert's process, taking care to use the minimum quantity of hypochlorite solution necessary to bleach the material. For an ordinary Indian bazaar sample of shellac the hypochlorite solution from 1 part of bleaching powder sufficed to bleach 6·5 parts of shellac. The alkaline solution was then cooled and acidified, without allowing the temperature to rise, when the shellac was precipitated as a granular solid which was collected, washed very thoroughly, suspended in water and treated with 1 part of sodium thiosulphate solution (10 per cent.) for each part of shellac. The shellac was collected, washed very thoroughly and air-dried. Samples of bleached shellac so produced have remained for the most part soluble in alcohol for over 3 years. The air-dried powder was kept in ordinary stoppered bottles in Cawnpore.

Sample prepared in February 1923; analysed April 1926.

  Insoluble in alcohol ... 9·5 per cent.
  Ash   ... nil.

Sample prepared in November 1924; analysed April 1926.

  Insoluble in alcohol ... 1·1 per cent.
  Ash   ... 0·5 ,,   ,,

We therefore claim that if the minimum quantity of hypochlorite is used for bleaching and the bleached product is precipitated in granular form, washed very thoroughly and treated with sodium thiosulphate to remove any absorbed chlorine, bleached shellac can be

prepared which will remain for the the most part soluble in alcohol for years.

In the course of these experiments it was noticed that it was difficult to remove all acid from the precipitated shellac.   The moist shellac pressed against litmus paper turned it red when the wash-water was neutral to litmus.

It was also noticed in the bleaching of specially dark lac, recovered from lac-dye, that it was necessary in bleaching to use solutions containing the minimum quantity of alkali. Under these conditions the hypochlorite exerted its maximum bleaching effect: If a larger quantity of alkali was used the bleaching was not so good and the bleached shellac was softer (melted at a lower temperature) than the original material. Probably the same would be the case in the bleaching of ordinary shellac.

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The Pinene Content of Indian Turpentine.

BY

· H. M. MULANY AND E. R. WASTON.

Simonsen (*J. Chem. Soc.*, 1920, *117*, 573) reported that the lower boiling fraction in Indian turpentine obtained from *Pinus longifolia*, amounting to 47 or 60 per cent. of the turpentine, consists mainly of a- and β-pinene. On this authority we used the fraction of Indian turpentine boiling at 155-160° as a source of pinene, and after some time we came to doubt whether it does consist mainly of pinene : we subjected it to a further examination to settle this point. It did not give any solid pinene hydrochloride whilst a sample of pinene obtained from French turpentine gave a direct yield of 27·5 per cent. Oxidised by Baeyer's method with potassium permanganate it gave a product that did not crystallise even after it had been fractionated under reduced pressure. It gave no pinene picrate by Tilden and Forster's method (*J. Chem Soc.*, 1893, *63*, 1388) or by a modification of this method, using molecular proportions of pinene and picric acid, whereas a sample of pinene obtained from British Drug Houses, Ltd., gave 16·6 per cent. of picrate by the modified method.

By Wallach's method (*Annalen*, 245, 251) it gave 1 per cent. of nitrosyl chloride whilst B. D. H. pinene gave a yield of 16·1 per cent. Oxidised by Henderson's method with mercury acetate (*J. Chem Soc.*, 1909, *95*, 289) it gave only 1 per cent. of sobrerol whilst a sample of pinene fractionated from May and Baker's oil of terebinth gave 5·5 per cent. Heated in an autoclave

it gave no dipentene whilst the sample of pinene obtained from May and Baker's oil of terebinth under the same conditions (250-260° for 1 hour) gave 65 per cent. of dipentene which readily gave the tetrabromide. It gave no terpin hydrate by Wallach's method with alcoholic nitric acid or by shaking with dilute sulphuric acid whereas pinene from May and Baker's oil of terebinth gave a 60 per cent. yield of terpin hydrate with dilute sulphuric acid under the same conditions (shaking 10 g. with 190 g. water and 10 g. of sulphuric acid continuously for a week).

The conclusion is that this fraction of 'Indian turpentine contains very little pinene. It contains some Δ^3-carnene as it gives the nitrosate, but the yield of the latter is not large. The product of oxidation by Baeyer's method gave an oxime melting at 121-2° whereas the oxidation product of pinene from foreign turpentine gave the oxime of l-pinonic acid, m.p. 131°.

The fraction boiling at 155-160° obtained from Indian turpentine is not large. One sample of first quality Bareilly turpentine gave 25 per cent. but another fresh sample gave only 8·6 per cent.

The final conclusion is that the pinene content of 'Indian turpentine must be very small.

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CAWNPORE.

Interaction of Sulphur Dichloride with Substances Containing the Reactive Methylene (-CH₂) Group or Substituted Methylene Group.

By

Kuverji Gosai Naik and Ganpat Vishram Jadhav.

The work was undertaken with a view (1) to study the reactivity of the hydrogen atoms of a methylene group situated between two carbonyl groups as in the case of substituted amides of malonic and methyl malonic acid, and (2) to throw light on the debated and vexed question of the constitution of sulphur dichloride.

The existence of a definite compound of the composition, SCl_2 has been repeatedly called in question (*J. Chem. Soc.*, 1870, *23*, 455; 1871, *24*, 1163, *Compt. rend.* 1878, *86*, 664; *Bull. Soc. chim.*, 1886, *45*, 867). SCl_2 has been regarded by some as a solution of chlorine in sulphur monochloride and by others as a compound in the state of partial dissociation. Costa (*Gazzetta*, 1890, *20*, 367) determined cryoscopically the molecular weight of the reddish brown liquid obtained by saturating the monochloride with chlorine below 0° and then removing the excess of chlorine by a current of carbon dioxide. The results of the determinations of molecular weight in benzene and in acetic acid solutions agree with the formula SCl_2. This view was challenged by Ruff and Fischer

(*Ber.*, 1903, *36*, 418) who assert that they got no evidence of the existence of the compound SCl_2? when they examined the composition of the liquid and the vapours at temperatures between $-10°C$ and $0°$. Böeseken (*Rec. trav. chim.*, 1905, *24*, 209) obtained diphenyl sulphide by the interaction of sulphur dichloride with benzene in the presence of anhydrous aluminium chloride at $0°$. This supports the view that at low temperatures sulphur dichloride possesses the formula SCl_2. At $60°$, however, the reaction takes a different course, chlorobenzene and thianthrene being the products formed. This is attributed to the decomposition of sulphur dichloride into the monochloride and chlorine, the latter then attacking the benzene nucleus.

Beckmann and his collaborators (*Zeit. physikal. Chem.*, 1909, *65*, 289) determined the molecular weights of the monochloride and the dichloride. They found that in liquid chlorine, at its boiling point, sulphur monochloride and sulphur dichloride have the molecular weights corresponding to the formulae S_2Cl_2 and SCl_2 respectively. They also arrived at the formula SCl_2 by means of cryoscopic determinations in xylene, *p*-xylene, ethylene dibromide, acetic acid and bromine solution. These results seem to have been confirmed by the work of Bergmann and Bloch (*Ber.*, 1920, *53*, [B], 977).

Malonanilide and malon di-*o*-tolylamide interact with SCl_2 as follows :—

$$\begin{array}{c} RNH.CO \\ {>}CH_2 +2SCl_2 \longrightarrow \\ RN\!H\!:\!CO \end{array} \quad \begin{array}{c} RNHCO \\ {>}C{<} \\ RNHCO \end{array}\begin{array}{c} S{-}Cl \\ \\ S{-}Cl \end{array} +2HCl \quad (I)$$

where R stands for the phenyl or the tolyl group.

In the case of both methyl-malonanilide and methyl-malon di-*o*-tolylamide only one hydrogen atom in the

2

reactive $-CH_2-$ group is available for interaction with sulphur dichloride, thus:—

$$\begin{array}{l} \text{RNH.CO} \\ \text{RNH.CO} \end{array} >C< \begin{array}{l} \text{H} \\ \text{CH}_3 \end{array} +SCl_2 \longrightarrow \begin{array}{l} \text{RNHCO} \\ \text{RNHCO} \end{array} >C< \begin{array}{l} \text{S—Cl} \\ \text{CH}_3 \end{array} + HCl \quad \text{(II)}$$
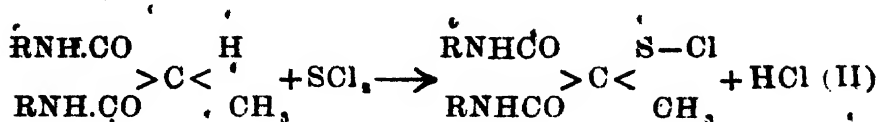
where R represents either the phenyl or the tolyl group.

From the above it will be evident that the total negativity of the adjoining group, $\cdot CO\cdot NHR$ (where R is either phenyl or tolyl) which influences the reactivity of the hydrogens of the methylene group is practically the same, and hence the reaction should follow the same course. Experiments have justified this.

It also appears that both the hydrogens of the methylene group in compound (I) are simultaneously attacked by sulphur dichloride. This is in contrast with what happens in the case of sulphur monochloride, where one molecule of the substituted amide reacts with one molecule of sulphur monochloride and not two (Naik, *J. Chem. Soc.*, 1921, *119*, 379). Thus in the case of sulphur monochloride the reaction follows the course:—

$$\begin{array}{l} \text{RNHCO} \\ \text{RNHCO} \end{array} >C< \begin{array}{l} \text{H} \\ \text{H} \end{array} \begin{array}{l} \text{Cl S} \\ \text{Cl S} \end{array} \longrightarrow \begin{array}{l} \text{RNHCO} \\ \text{RNHCO} \end{array} >C< \begin{array}{l} \text{S} \\ \text{S} \end{array} + 2HCl \quad \text{(III)}$$

where R is either the phenyl or tolyl group.

It is interesting to observe that, in general, the dithioketones obtained by the interaction of sulphur monochloride with some of the substituted amides are extremely stable (Naik, *J. Chem. Soc.*, 1921, *119*, 1231), whereas the compounds obtained by the action of sulphur dichloride are unstable, when treated with fuming nitric

acid. In the case of compound (I) the reaction proceeds as follows :—

$$\begin{array}{c}RNHCO \\ RNHCO\end{array}>C<\begin{array}{c}S-Cl \\ S-Cl\end{array} \xrightarrow{\text{nitration}} \begin{array}{c}R_1(NO_2)NHCO \\ R_1(NO_2)NHCO\end{array}>CH_2$$
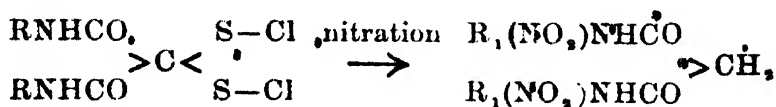
where R_1 stands for phenylene or tolylene group.

The products obtained from malon di-n-propylamide and malon di-naphthylamides ($a-$ and $\beta-$) belong to the same class. The reaction follows the course given below.:—

$$\begin{array}{c}R_1NHCO \\ R_1NHCO\end{array}>C<\begin{array}{c}H \\ H\end{array}+Cl-S-Cl \longrightarrow \begin{array}{c}R_1NHCO \\ R_1NHCO\end{array}>C<\begin{array}{c}H \\ S-Cl\end{array}+HCl \text{ (IV)}$$

(IV)
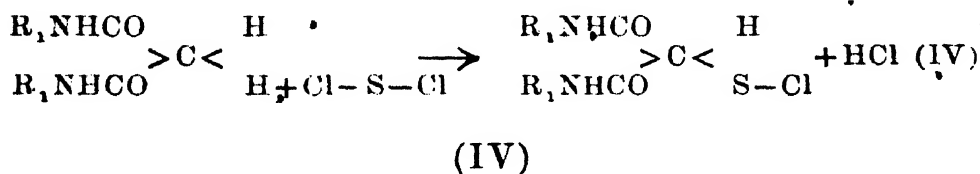
where R_1 stands for propyl group.

$$\begin{array}{c}RNHCO \\ RNHCO\end{array}>C<\begin{array}{c}H \\ H\end{array}+Cl-S-Cl \longrightarrow \begin{array}{c}RNHCO \\ RNHCO\end{array}>C<\begin{array}{c}H \\ S-Cl\end{array}+HCl \text{ (V)}$$

(V)
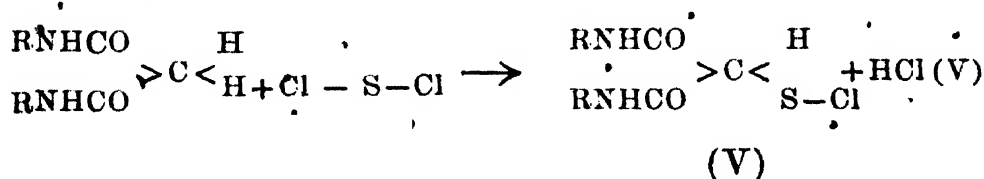
where R stands for a- or β-naphthyl group.

Here the total negativity of the group ·CO·NHR (where R is the propyl or naphthyl group) is reduced to a level which admits of the reactivity of only one of the hydrogens of the methylene group. · In such cases it is but natural to expect the above course of the reaction.

These compounds are also unstable and lose all their sulphur and chlorine when nitrated, thus :—

$$\begin{array}{c}RNHCO \\ RNHCO\end{array}>C<\begin{array}{c}H \\ S-Cl\end{array} \xrightarrow{\text{Nitration}} \begin{array}{c}R_1(NO_2) \\ R_1(NO_2)\end{array}>CH_2$$
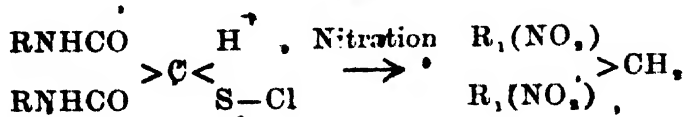
where R_1 stands for naphthylene group.

Finally, in the cases of malon di-*p*-tolylamide, malon di-benzylamide and methyl-malon-di-*p*-tolylamide the reaction with sulphur dichloride proceeds further and very unstable compounds containing excess of chlorine are produced. In the case of methyl-malon-di-*p*-tolylamide the methyl group also is attacked, thus :—

$$\begin{matrix} RNHCO \\ RNHCO \end{matrix} \!\!>\!C\!<\!\! \begin{matrix} H \\ H \end{matrix} + 2SCl_2 = \begin{matrix} RNHCO \\ RNHCO \end{matrix} \!\!>\!C\!<\!\! \begin{matrix} Cl \\ SCl \end{matrix} + 2HCl + S \quad (VI)$$
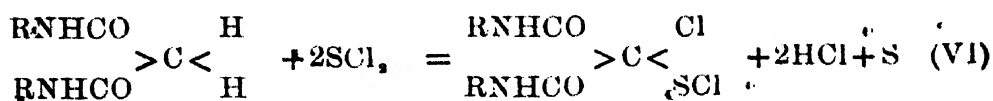
where R is a *p*-tolyl or benzyl group.

$$\begin{matrix} C_7H_7NHCO \\ C_7H_7NHCO \end{matrix} \!\!>\!C\!<\!\! \begin{matrix} CH_3 \\ H \end{matrix} + 2SCl_2 = \begin{matrix} C_7H_7NHCO \\ C_7H_7NHCO \end{matrix} \!\!>\!C\!<\!\! \begin{matrix} CH_2 \\ S \end{matrix} + 2HCl$$
$$Cl \wedge Cl$$
$$(VII)$$
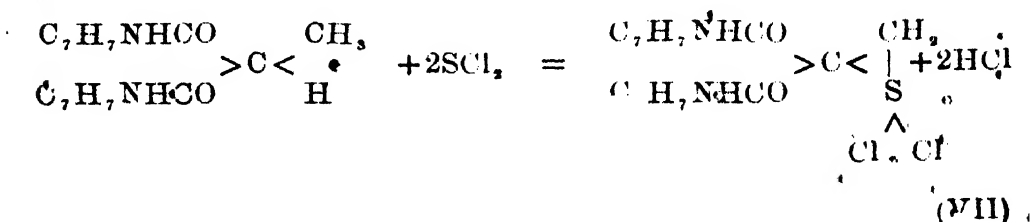
The above products are stable only in a desiccator over sulphuric acid. In moist air they decompose, the original amide being obtained, with the evolution of hydrogen chloride and deposition of sulphur. It is interesting to observe that the tolyl compound (VI) on nitration loses all its sulphur and chlorine forming

$$[(NO_2)C_7H_6NH.CO]_2CH_2$$

The constitutions assigned to the above compounds follow from the following considerations :—

(1) That the hydrogen atom or atoms attacked by the dichloride are not those from the aromatic nuclei is evident from the course of the reaction in case (IV) where no such aromatic nuclei are present.

(2) The two hydrogen atoms eliminated are not those which were originally attached to the two nitrogen atoms ;

because, if that was so, the course of the reaction in every case ought to have been the same, for every one of the amides has two available ·CO·NHR groups.

(3) On reduction with alkaline hydrosulphide, say, in the case of (I), the original amide is obtained.

$$(ClS)_2C : (CONHC_7H_7)_2 + 4H_2 = CH_2(CONHC_7H_7)_2 + 2HCl + 2H_2S$$
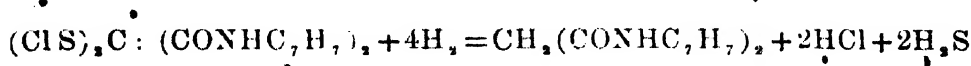
(4) That the original amide is obtained in the case of (VI) and (VII) in the presence of even a trace of moisture is sufficient to show that the reaction takes place with the hydrogens of the methylene group; because, if the interaction had taken place with the hydrogens of the aromatic nucleus, the substituted halogens could not be easily removed with water.

Apart from the light which the study of these reactions throws on the reactivity of the group, $CO\text{-}CH_2\text{-}CO$, another and a very important bearing of this work is in relation to the constitution of sulphur dichloride. The previous work done by one of us (Naik, *loc. cit.*) has tentatively shown that sulphur monochloride reacts in two forms :

$$\begin{array}{ll} \text{Cl---S} \\ \quad | \qquad\qquad \text{(I)} \qquad\qquad\qquad S=S<\begin{array}{l}\text{Cl}\\\text{Cl}\end{array} \qquad \text{(II)} \\ \text{Cl---S} \end{array}$$

and it is only in the case of (I) that stable disulphides are obtained. It was suggested in the beginning that sulphur dichloride is a mixture of monochloride and chlorine, or of tetrachloride and monochloride (*Ber.*, 1903, *36*, 418). If this had been the case, in none of the above reactions could there have been a possibility of obtaining a definite class of compounds. The monochloride which was supposed to be one of the constituents which go to form the dichloride, ought to have contributed stable dithioketones, as was found out by Naik (*loc. cit.*).

The other constituent of sulphur dichloride, *viz.*, chlorine ought to have easily chlorinated the aromatic nucleus, and given aromatic chloro-compounds. But in no case were nuclei substituted halogen derivatives obtained. On the other hand, the compounds obtained possessed a separate identity of their own. It is, therefore, beyond doubt that sulphur dichloride did neither react as a mixture of sulphur monochloride and chlorine nor a mixture of sulphur tetrachloride and monochloride, but it is a definite chloride of sulphur having the formula SCl_2.

EXPERIMENTAL.

The reactions were carried out in benzene solution. Under the conditions of the experiments there was no interaction between the solvent and the sulphur dichloride. In most cases the product of reaction separated from the cold solution in the crystalline form. Dry materials were always used, and when a reaction mixture had to be left overnight, precautions were taken against the entrance of moisture.

Sulphur Dichloride and Malon-anilide.

Malon anilide (3 g.) was mixed with dry benzene (20 c.c.), and sulphur dichloride (6g.) was added to the mixture. The reaction started at once and hydrochloric acid gas was evolved. The flask was corked with calcium chloride tube to avoid moisture and was left overnight. Next day it was heated under reflux over a sand-bath for four hours. As soon as benzene began to boil, copious fumes of hydrochloric acid gas were thrown out. The clear solution on standing deposited feathery needle-shaped crystals. They were filtered and washed with dry petroleum. They were found to be very soluble in acetic

acid, fairly soluble in alcohol, acetone, benzene ,and chloroform, sparingly soluble in ' light petroleum. On crystallisation. from benzene the substance melted at 164-165°. (Found: $Cl = 18\cdot69$; $S = 16\cdot72$. $C_{15}H_{12}N_2O_2$ S_2Cl_2 requires $Cl = 18\cdot35$; $S = 16\cdot54$ per cent.).

Nitration.—The compound (1 g.) was gradually added to fuming nitric acid (7 c.c.). Nitrogen peroxide came off and the mixture became hot. After some time air was blown into the acid to remove the fumes of nitrogen peroxide. The colourless liquid was then slowly added to water, when a yellow solid separated. It was filtered and washed completely with water. It shrank at 81° and melted with decomposition at 90°. (Found: $N = 16\cdot10$. $C_{15}H_{12}N_4O_6$ requires $N = 16\cdot28$ per cent.).

Sulphur Dichloride and Malon-di-o-tolylamide.

Malon-di-*o*-tolylamide (2 g.) was mixed with dry benzene (20 c.c.), and sulphur dichloride (5 g.) was added to the mixture. The reaction was vigorous and copious fumes of hydrogen chloride were formed. The mixture was refluxed over a sand-bath for three hours. On standing the clear liquid deposited white silky needles. They were filtered and washed with dry petroleum. They were soluble in benzene, alcohol, acetone, carbon tetrachloride and chloroform, and sparingly soluble in ether and petroleum. They were crystallised from hot benzene; m. p. 160-161°. (Found: $Cl = 17\cdot34$; $S = 15\cdot55$. $C_{17}H_{16}N_2O_2S_2Cl_2$ requires $Cl = 17\cdot11$; $S = 15\cdot43$ per cent.).

Reduction.—The substance (1 g.) was dissolved in alcohol, and ·10 c.c. of an aqueous solution of sodium hydrogen sulphide (A solution was made by saturating 1·5 g. of caustic soda with hydrogen sulphide in a small quantity of water. To it caustic soda (5·7 g.) dissolved in a small quantity of water was added and the whole

made up to 30 c.c.) was gradually added to it, when a brown solution was obtained. The solution was diluted with water, and the solid obtained was washed with water. It was crystallised from glacial acetic acid; m. p. 190-191°. It contained neither chlorine nor sulphur and was identified as the original amide.

Nitration.—The compound (1 g.) was gradually added to 10 c.c. of fuming nitric acid when fumes of nitrogen peroxide were thrown out. The liquid, after somtime, was warmed a little on a water-bath. After blowing air through the acid, the nearly colourless liquid was diluted with water and the reddish mass obtained was filtered and washed with cold water. It shrank at 75° and melted with decomposition at 85°. (Found : N = 14·88. $C_{17}H_{19}O_6N_4$ requires N = 15·05 per cent.).

Sulphur Dichloride and Methyl-malonanilide.

Methyl malonanilide (2 g.) was added to dry benzene (15 c.c.), and sulphur dichloride (4 g.) was then added to it. The reaction mixture was finished up as in the preceding case. The solid was soluble in acetic acid, alcohol, acetone, benzene and chloroform, and sparingly soluble in ether and petroleum ; m. p. 132°. (Found: Cl = 10·39; S = 9·27. $C_{16}H_{15}N_2O_2SCl$ requires Cl = 10·61; S = 9·55 per cent.).

Sulphur Dichloride and Methyl-malon-di-o-tolylamide.

Methyl-malon-di-o-tolylamide (2 g.) was put in 15 c.c. of dry benzene and sulphur dichloride (4 g.) was added to it. The reaction mixture was heated under reflux over a sand-bath for three hours, after keeping it at ordinary temperature for some time. On standing, same crystals were deposited and more solid was obtained on dilution

with dry petroleum. The mass was crystallised from benzene; m. p. 150° (Found: Cl=9·39; S=8·69. $C_{18}H_{19}N_2O_2SCl$ requires Cl = 9·79; S = 8·82 per cent.).

Sulphur Dichloride and Malon-di-a-naphthylamide.

Malon di-a-naphthylamide (3 g.) was added to 20 c.c. of dry benzene. Sulphur dichloride (7 g.) dissolved in a little benzene was then added to the mixture. After some time, the mixture was refluxed over a sand-bath for three hours when hydrogen chloride ceased to evolve. When benzene began to boil, the liquid assumed green colour. On standing the solution deposited a solid which was filtered and washed with dry petroleum. The white mass soon began to be blue on the surface. It was therefore put in a desiccator. It was crystallised from benzene. It became blue. It was soluble in acetic acid, acetone, benzene and carbon tetrachloride, and sparingly soluble in ether and petroleum. It melted with decomposition at 145°. (Found: Cl=8·63; S=8·09. $C_{23}H_{17}N_2O_2SCl$ requires Cl=8·44; S = 7·6 per cent.).

Sulphur Dichloride and Malon-di-β-naphthylamide.

The amide (5 g.) was added to 50 c.c. of dry benzene and sulphur dichloride (10 g.) was added to it. Hydrogen chloride was at once thrown out. The mixture was refluxed over a sand-bath for four hours, but the product was insoluble in benzene. On cooling the solid was filtered and washed. It was sparingly soluble in alcohol, acetone and ether, and fairly soluble in boiling acetic acid, from which it came down as an amorphous yellowish powder. It melted with decomposition at 230°—31°. (Found: Cl=8·55;. S = 7·37. $C_{23}H_{17}N_2O_2SCl$ requires Cl=8·44; S=7·61 per cent.).

3

Nitration.—The compound (1 g.) was gradually added to 10 c.c. of fuming nitric acid. Copious fumes of nitrogen peroxide were thrown out. The mixture was heated on a water-bath for some time and then air was blown into the hot mixture to remove the fumes. It was then diluted with cold water and the yellowish solid obtained was filtered and washed. It shrank at 175° and melted with decomposition at 185°. (Found: $N = 12 \cdot 45$. $C_x H_{16} N_4 O_6$ requires $N = 12 \cdot 6$ per cent.).

Sulphur Dichloride and Malon-di-n-propylamide.

The amide (2 g.) was added to 25 c.c. of dry benzene and sulphur dichloride (4 g.) was then added to it. The reaction started at once and the reaction mixture became hot. The flask was corked with a calcium chloride tube and left overnight. Next day it was refluxed over a sand-bath for about an hour and then concentrated, when a solid was deposited. It was filtered and washed with dry petroleum. On slow evaporation of petroleum the white solid began to smell of hydrochloric acid and became pasty. It was then placed in a desiccator over caustic soda for several days. Afterwards it was crystallised from dry benzene and the solid was washed with a mixture of ether and petroleum. It is soluble in alcohol and benzene, and sparingly soluble in chloroform, ether and petroleum; m. p. 141—142°. (Found: $Cl = 13 \cdot 80$; $S = 12 \cdot 50$. $C_9 H_{17} N_2 O_2 SCl$ requires $Cl = 14 \cdot 06$; $S = 12 \cdot 67$ per cent.).

Sulphur Dichloride and Malon-di-p-tolylamide.

The amide (4 g.) was mixed with 25 c.c. of dry benzene and sulphur dichloride (8 g.) was added to the mixture. The reaction started at once with the evolution of hydrogen chloride. The flask was corked with a

calcium chloride tube and left overnight at room tempera-ture. Next day it was refluxed over a sand-bath for about four hours. On cooling the clear solution deposited white crystals which were filtered and washed with dry petroleum. They were soluble in acetic acid, alcohol, acetone, benzene, carbon disulphide and chloroform. The solid was crystallised from benzene ; m. p. 156°. (Found: Cl=18.16 ; S=8.78. $C_{17}H_{16}N_2O_2SCl_2$ requires Cl = 18.54 ; S = 8.35 per cent.).

The compound when put in ordinary air was found to smell of hydrochloric acid after some days. This went on for about two months, after which period the com-pound assumed a yellowish tint. It was insoluble in benzene and was crystallised from glacial acetic acid ; m. p. 247°. It was found to contain neither sulphur nor chlorine and was identified as the original amide. The compound is stable when put in a desiccator over concen-trated sulphuric acid.

Nitration :—The compound (1 g.) was gradually added to 8 c.c. of fuming nitric acid. Fumes of nitrogen pero-xide were thrown out when the substance was being added. After some time air was blown into the acid and the nearly colourless solution was diluted with water, when a yellow mass was obtained. It shrank at 85° and melted with decomposition at 120°. (Found; N = 14.72. $C_{17}H_{18}N_4O_6$ requires N = 15.05 per cent.).

Sulphur Dichloride and Malon-di-benzylamide.

The amide (3 g.) was taken with 25 c.c. of dry ben-zene and sulphur dichloride (6 g.) was added to the mixture. The reaction mixture was corked with a cal-cium chloride tube and left overnight at room. tempera-ture. Next day it was refluxed over a sand-bath for six

hours when hydrogen chloride ceased to evolve. The clear solution on standing deposited white silky needle-shaped crystals. They were filtered and washed with dry petroleum. They were soluble in acetic acid, alcohol, acetone, benzene and chloroform. The mass was crystallised from boiling benzene, m. p. 149—150°. (Found: $Cl = 18\cdot26$; $S = 8\cdot82$. $C_{17}H_{16}N_2O_2SCl_2$ requires $Cl = 18\cdot54$; $S = 8\cdot35$ per cent.).

This product also decomposed as in the case of malon di-*p*-tolylamide and the original amide was obtained in this case too.

Sulphur Dichloride and Methyl-malon-di-p-tolylamide.

The amide (4 g.) was put in 25 c.c. of dry benzene and sulphur dichloride (8 g.) was added to the mixture. The flask was corked with a calcium chloride tube and left overnight at room temperature. Next day it was refluxed over a sand-bath for three hours. The clear solution on standing deposited crystals. They were filtered and washed with dry petroleum. They were soluble in acetic acid, alcohol, benzene, acetone and chloroform, and sparingly soluble in ether and petroleum. The mass was crystallised from benzene, m. p. 157—158°. (Found: $Cl = 18\cdot23$; $S = 7\cdot88$. $C_{18}H_{18}N_2O_2SCl_2$ requires $Cl = 17\cdot88$; $S = 8\cdot06$ per cent.).

This compound also decomposed as in the two previous cases. The decomposition product was insoluble in benzene and therefore it was crystallised from glacial acetic acid, m. p. 240°. It was identified as the original amide. The compound was stable when put in a desiccator over concentrated sulphuric acid.

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The Isomeric Transformation of *allo*-Cinnamylidene Acetic Acid into the Normal Form with Iodine as Photo-catalyst, in Methyl Alcohol Solution.

Part II.

By

Jnanendra Chandra Ghosh

and

Munindra Nath Mitra.

Liebermann discovered that *allo*cinnamylidene acetic acid is very slowly transformed into the normal form under the influence of light, but in presence of iodine this photochemical transformation is very rapid (*Ber.*, 1895, 28, 1446). In a previous paper by Ghosh and Gupta the velocity of the above transformation in chloroform solution has been studied (*J. Indian Chem. Soc.*, 1925, 2, 241). In the present paper the results obtained with methyl alcohol as solvent are given.

The method for the estimation of the quantity of *allo*-form which has been changed into the normal form as described in the previous paper had to be considerably modified in this case. The following experimental procedure was finally adopted: 2 c. c. of the alcohol solution containing the *allo*-acid were taken out and poured into a small stoppered conical flask containing perfectly anhydrous sodium thiosulphate. The iodine immediately reacted with sodium thiosulphate and the

solution became colourless. The flask was then introduced into a vacuum desiccator connected with an oil-pump of large capacity. The alcohol evaporated rapidly at a temperature somewhat below 30° and the *allo*-acid during this process of evaporation did not undergo any further transformation into the normal form. Three c. c. of dry benzene was then added and shaken vigorously to dissolve the acids in the solid residue. The benzene solution was then poured into a long stoppered tube and kept overnight in a thermostat. One c. c. of the clear liquid was sucked up by a pipette through a plug of glass wool fitted at its lower end, and titrated with baryta solution. The *allo*-acid is freely soluble in benzene but the normal acid is only slightly soluble. Table I gives the solubility of the normal acid in benzene at different temperatures in gram moles per c. c.

TABLE I.

Temperature.	Solubility × 10⁶
15°	24·5
22°	30·4
30°	44·4
35°	57·5

From the solubility curve of normal acid in benzene, the quantity of normal acid at the temperature of the thermostat was determined and the difference between the total quantity of acid in 1 c. c. of benzene and the solubility of normal acid gave the amount of *allo*-acid in the solid residue of the conical flask which has dissolved in one c. c. of benzene. The total *allo*-acid in the residue is three times this quantity and was present in 2 c. c. of the alcohol solution.

The experimental arrangement is essentially the same as given in the previous paper. A hundred candle power point-o-lite lamp was used as the source of light and convex lenses of different focal lengths were used to obtain parallel beams of light of varying intensity. The light was passed through a filter of copper sulphate solution 10 cm. thick to cut off heat radiations and then entered the reaction vessel (4×4×1 cm.) enclosed in a double jacketed copper box with a glass window to admit light. This copper box was maintained at constant temperature by circulating water from a thermostat. The intensity of incident radiation and the fraction of incident light absorbed by the reacting solution was measured by a Moll thermopile and galvanometer calibrated by means of a Hefner lamp.

The End-point of Reaction.—It was found that the transformation of *allo*-acid into the normal form does not proceed to completion in methyl alcohol solution. The reaction stops after ninety per cent. of the *allo*-acid has been converted into the normal variety. This percentage conversion was found to be independent of (1) concentration of iodine, (2) the intensity of incident light, and (3) almost independent of temperature. Such behaviour is indeed expected if both iodine and light act simply as catalysts. The negligible effect of temperature on the percentage conversion at equilibrium is to be ascribed to the fact that the energy change in this transformation is very small. The exact value of the heat of transformation in this case is not known, but for the corresponding change of *allo*-furfuraldehyde acrylic acid into the normal form the heat of transformation is only 4·3 calories (Roloff, *Zeit. physikal. Chem.*, 1898, 26, 337).

The simple equation, $k = \dfrac{1}{t_2 - t_1} \cdot \log \dfrac{a}{a - x}$ for the velocity

of a monomolecular reaction cannot be applied to this case. We have rather to use the more complicated equation for homogeneous unimolecular opposing reaction

$$k = k_1 \frac{a}{z} = \frac{1}{t_2 - t_1} . \log \frac{z}{z - x_2}$$

where a is the initial concentration of *allo*-acid, z is the concentration of normal acid at equilibrium, and x is the quantity of *allo*-acid converted into normal form in time t; in the following tables

$$k' = \frac{1}{t} \log \frac{z}{z - x} \quad \text{and} \quad k'' = \frac{1}{t_n - t_1} . \log \frac{z - x_1}{z - x_n} .$$

TABLE II.

Solvent—*Methyl alcohol.*

$I_0 = 133/138$ Hefner: Initial concentration of *allo*-acid, 0.2794 N.

Temp.$= 32°$: Concentration of iodine $= 0.001$ N.

Time.		C. c baryta solution equivalent to		k'	k''
		conc. of allo-acid + dissolved normal acid	conc. of allo-acid.		
0	0	50·8	50·8	...	...
t_1	80	49·66	39·16	·0037	...
t_2	110	43·28	32·78	·0046	·0069
t_3	140	37·39	26·89	·0053	·0074
t_4	174	32·92	22·42	·0069	·0074
					Mean ·0072

TABLE III.

Concentration of iodine = 0·00202 N.

Time.	Concentration of *allo*- acid in c. c. baryta solution.	k'	k''
0	57·87	......	......
45	36·27	·0119	......
75	23·86	·0141	·0174
100	17·51	·0149	·0173
120	14·13	·0153	·0173
			Mean ·0173

TABLE IV.

Concentration of iodine = 0·006 N.

Time.	Concentration of *allo*-acid in c.c. baryta solution.	k	k''
0	60·88	......	......
21	37·03	·0271	......
30	25·17	·0351	·0536
46	14·36	·0411	·0527
61	9·63	·0449	·0541
75	7·81	·0469	·0534
			Mean ·0535

4

TABLE V.

Concentration of iodine $= 0{\cdot}01179\ N.$

Time.	Concentration of *allo*-acid in c.c. baryta solution.	k'	k''
0	58·09	......	......
16	39·80	·0269	......
25	24·35	·0416	·0674
35	14·90	·0409	·0692
45	10·27	·0557	·0699
			Mean ·0688

TABLE VI.

Concentration of iodine $= 0{\cdot}0155\ N.$

Time.	Concentration of *allo*-acid in c.c. baryta solution	k'	k''
0	47·32	......	......
13	·32·70	·0322	......
23	20·17	·0442	·0593
33	13·78	·0469	·0564
43	9·82	·0495	·0568
53	7·48	·0520	·0580
			Mean ·0576

TABLE VII.

Concentration of iodine $= 0.024\ N$.

Time.	Concentration of *allo*-acid in c. c. baryta solution.	k'	k''
0	22·6	......	......
17	14·71	·0288	......
32	9·76	·0311	·0338
47	6·71	·0322	·0343
62	4·83	·0334	·0350
84	3·69	·0315	·0322
			Mean ·0338

TABLE VIII.

Concentration of iodine $= 0.0320\ N$.

Time.	Concentration of *allo*-acid in c.c. baryta solution.	k'	k''
0	83·1	......	......
20	53·07	·0235	......
35	39·44	·0251	·0269
50	32·10	·0229	·0225
65	25·87	·0223	·0218
80	23·34	·0200	·0189
			Mean ·0225

TABLE IX.

Concentration of iodine $= 0.048$ N.

Time.	Concentration of allo-acid in c. c. baryta solution.	k'	k''
0	83·1	...	...
20	66·5	·0121	...
35	55·5	·0131	·0146
50	47·5	·0124	·0134
70	41·5	·0115	·0114
			Mean ·0131

It will be noticed from Tables II–IX that for smaller concentrations of the catalyst iodine, the const. k' continually increased indicating that in these experiments the reaction passes through a period of induction. As, however, the concentration of iodine increased to 0.024 N the induction period disappeared and identical values of velocity constant were obtained from the beginning of the reaction. That there is this disturbance at the beginning of the reaction is also evident from the fact that the values of k'', calculated from data obtained after some time has elapsed after exposure to light, are all identical within the limits of experimental error. The variation of the velocity constant k'', with the concentration of iodine is given in diagram I (a). It will be noticed that the constant increases very rapidly as the concentration of iodine increases, passes through a maximum and then diminishes. This point will be further discussed later on.

It is important to mention here that the above data were obtained by exposing to light a mixture of freshly prepared solutions of allo-acid and iodine in methyl alcohol.

Fig. 1.
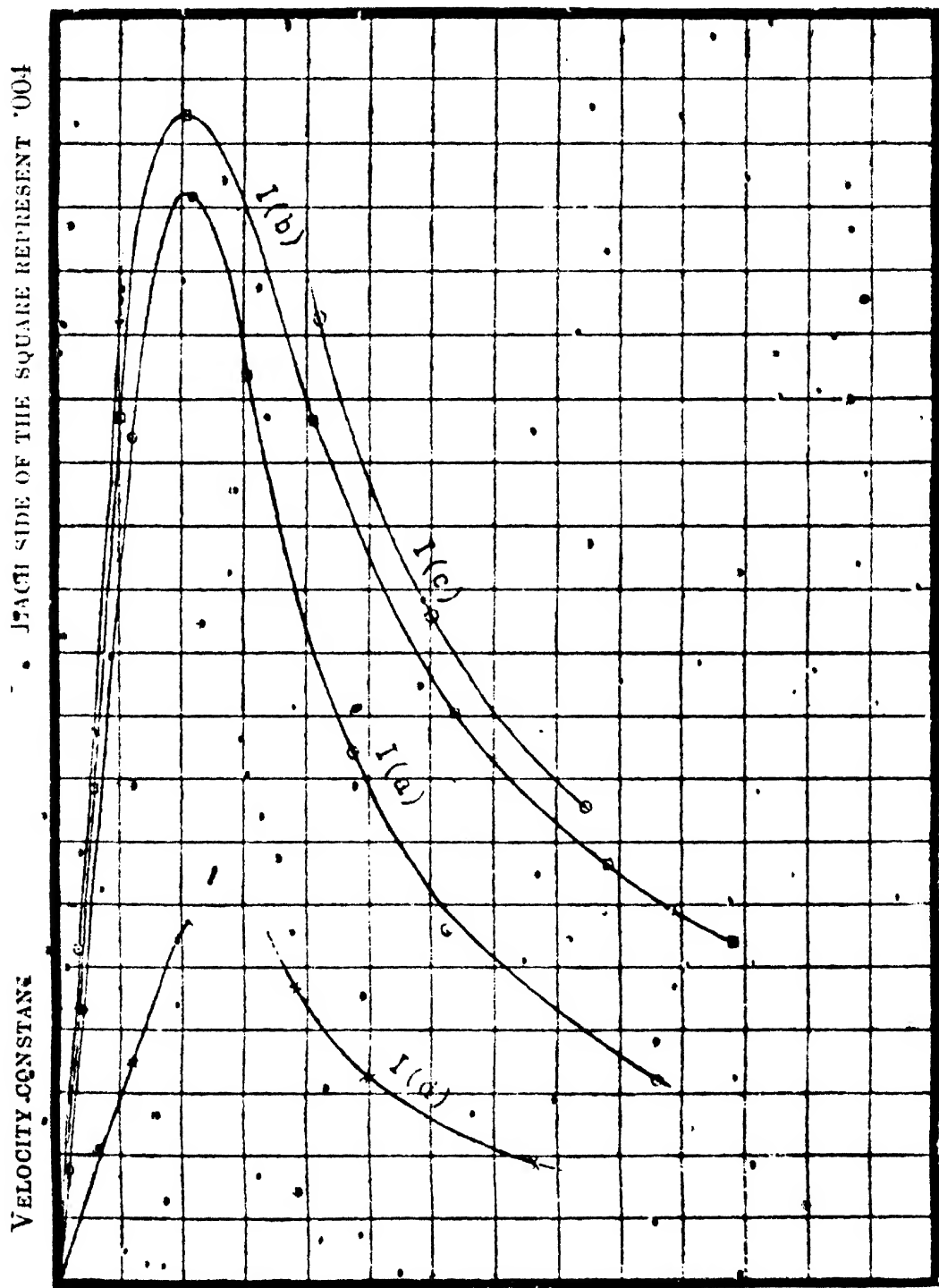
CONCENTRATION OF IODINE
EACH SIDE OF THE SQUARE REPRESENTS ·005 N.

The Effect of 'ageing' of the Solutions on the Velocity Constants.

In course of performing the experiments recorded above it was noticed that the results obtained were not always concordant. This puzzling phenomenon was ultimately traced to the effect of the 'ageing' of the solutions of the *allo*-acid and iodine. It was found that, if the reaction was started by mixing and exposing to light the methyl alcohol solutions of iodine and *allo*-acid immediately after they were separately made, the velocity constants obtained under identical conditions of concentration, temperature and light intensity were always the same. But if old solutions are mixed together and exposed to light the values of velocity constants were always less.

Initial conc. of *allo*-acid, 14.23×10^{-2} N.
Concentration of iodine, 1.5×10^{-2} N.
Light intensity, 133.138 Hefner.
Temperature, 32°.

TABLE X.

Solutions mixed and exposed to light 30 min. after preparation.

Time.	Conc. of allo-acid in c.c. baryta solution.	k'	k''
0	41.52	......	......
15	26.26	.0350	......
25	14.83	.0409	.0727
35	9.56	.0552	.0704
45	6.82	.0587	.0704
			Mean .0712

TABLE XI.

Solutions mixed and exposed to light 22 hours after preparation.

Time.	Conc. of *allo*-acid in c.c. baryta solution.	k'	k''
0	41·68	......	......
16	23·96	·0342	......
26	16·50	·0428	·0474
36	12·03	·0435	·0462
46	8·95	·0449	·0474
56	7·17	·0451	·0472
			Mean ·0471

TABLE XII.

Solutions mixed and exposed to light $44\frac{1}{2}$ hours after preparation.

Time.	Conc. of *allo*-acid in c.c. baryta solution.	k'	k''
0	41·91	......	......
18	23·06	·0373	......
28	16·84	·0382	·0396
38	12·79	·0382	·0391
48	9·57	·0400	·0409
58	7·78	·0400	·0409
			Mean ·0401

Fig. II.

EACH SIDE OF THE SQUARE REPRESENTS ·002

VELOCITY CONSTANT

TIME IN HOURS

EACH SIDE OF THE SQUARE REPRESENTS 5 HOURS
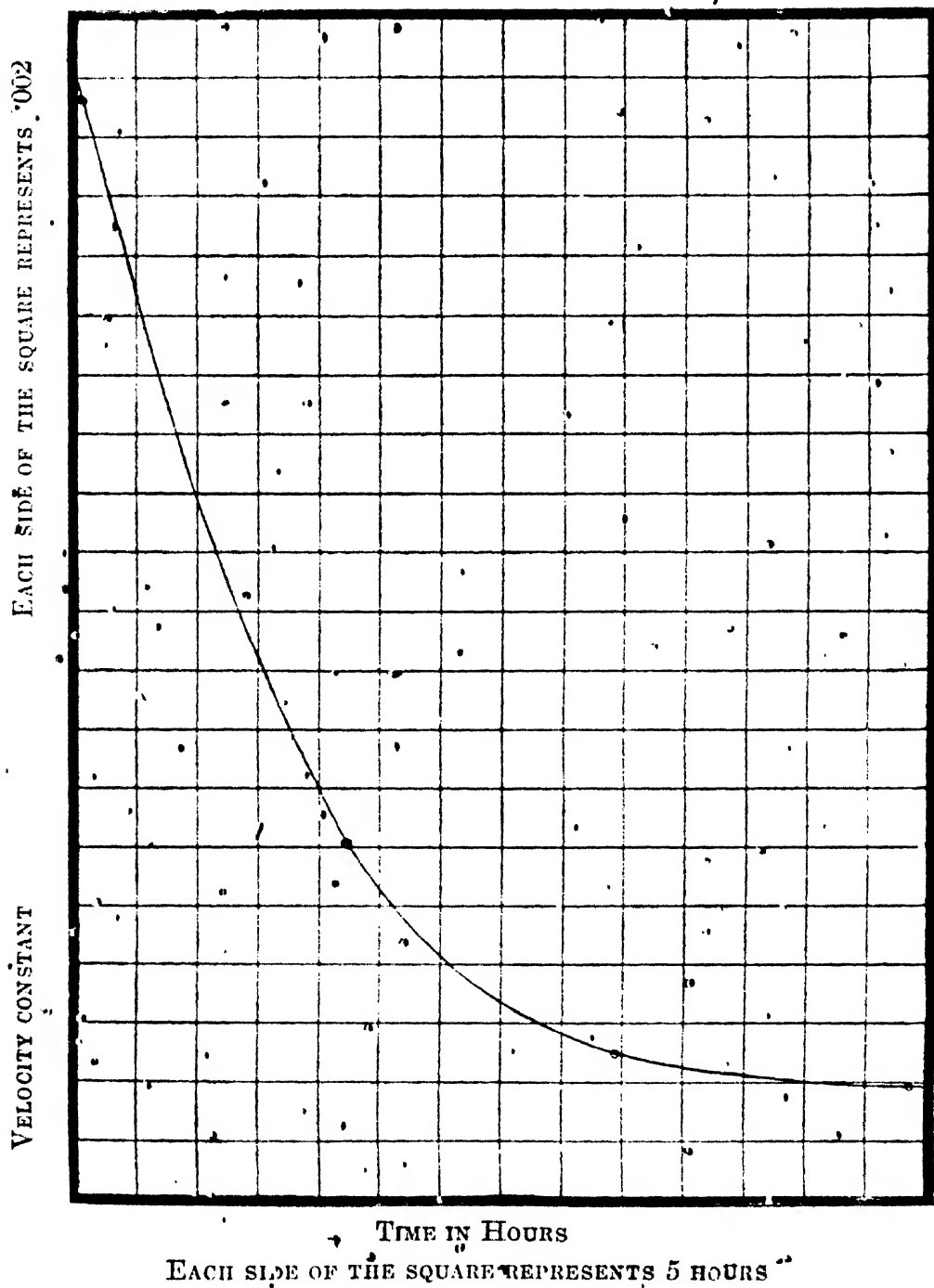
TABLE XIII,

Solution mixed and exposed to light· 68¾·hours after preparation.

Time.	Conc. of *allo*-acid in c. c baryta solution.	k'	k''
0	41·98	......	......
20	24·27	·0315	......
38	13·88	·0359	·0391
51	10·21	·0361	·0391
60	8·47	·0366	·0386
			Mean ·0389

It will be seen that the values of k'' are identical for the same experiment, but vary with the ageing of the solution. The results are plotted in Fig. II. k'' diminishes with time in an asymptotic way, its value after a certain time becoming more or less constant. It will be further noticed that the values of k' as noted before are different for the same experiment for freshly·prepared solutions. But with the ageing of the solutions, the values of k' become identical indicating that the disturbing influences which were responsible for the induction period have disappeared. The nature of these disturbing influences is not clear at present.

Effect of Initial Concentration of the allo-*Acid on the Velocity of Reaction.*

It was noticed in a previous paper by Ghosh and Gupta (*loc. cit.*) that other conditions being the same, the monomolecular velocity coefficient in chloroform· solutions diminishes with increase in the initial concentration

of the *allo*-acid.　　Similar results have been obtained with methyl alcohol as solvent, as will be clear from the Table XIV and curve I(*b*) where the results are given diagramatically.

TABLE XIV.

Initial concentration of *allo*-acid, $14.23 \times 10^{-?} N.$
Temp. $= 32°$.　　Intensity $= 133/138$ Hefner.

Concentration of iodine.	$.0027N$	$.0053N$	$.01066N$	$.0212N$	$.032N$	$.044N$	$.0543N$
Velocity coefficient, k''.	$.0316$	$.0549$	$.0738$	$.0547$	$.0362$	$.0268$	$.0218$

It will be noticed that the curve I (*b*) remains parallel to curve I(*a*) and is always *above* it.

Influence of Temperature on the Velocity of Reaction.

It has been pointed out before that the percentage of conversion of the *allo*-acid into normal form, when equilibrium was reached, did not vary perceptibly with temperature. The influence of temperature on velocity coefficient was also quite small.

TABLE XV.

Temp. $= 38°$,　　Intensity $= 133/138$ Hefner.

Initial conc. of *allo*-acid $= 14.23 \times 10^{-2} N.$

Conc. of iodine.	$.00164N$	$.0054N$	$.0211N$	$.0311N$	$.0422N$
Velocity coefficient, k''	$.0213$	$.0611$	$.0613$	$.0404$	$.0304$

The results are given in curve I (c).

The Influence of Incident Light on the Velocity of Transformation.

TABLE XVI.

Initial conc. of *allo*-acid $= 14 \cdot 23 \times 10^{-2}$ N.

$I_0 = 32/138$ Hefner.   Temp. $= 38.°$

Conc. of iodine.	·0062N.	·0106N.	·0190N.	·0248N.	·03816N.
Velocity coefficient, k''	·0139	·023	·0186	·0130	·0075

The results are graphically represented in curve I (d).

TABLE XVII.

Initial conc. of *allo*-acid $= 14 \cdot 23 \times 10^{-2}$ N;

$I_0 = 25/138$ Hefner ;   Temp. $= 38°$.

Conc. of iodine		·00878N.	·01756N.
Velocity coefficient, k''	...	·0154	·0160

In Table XVIII are given the values of velocity coefficients for different intensities of incident radiation, other experimental conditions remaining the same.

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TABLE XVIII.

Initial concentration of *allo*-acid, 14.23×10^{-2} N. Temperature, 38°.

Conc. of iodine.	Ratios of intensities.	Ratios of velocity coefficient.
·00878 N	32,35 = 1·28	·0196/·0154 = 1·27
·1756 N	32,25 = 1·28	·02/·016 = 1·25
·020 N	133/32 = 4·16	·0636/·0176 = 3·61
·0248 N	133/32 = 4·16	·0516/·0180 = 3·97
·030 N	133/32 = 4·16	·0420/·0104 = 4·04
·038 N	133/32 = 4·16	·0332/·0075 = 4·43

It will be seen that the ratio of the velocity co-efficients is approximately proportional to the ratio of. incident intensities.

Estimation of the Number of Molecules of allo- *acid transformed per Quantum of Light absorbed.*

In chloroform solution, one quantum of light absorbed by iodine transformed under different conditions of experiment between 1 to 2·8 molecules of *allo*-acid. In methyl alcohol solution, the reaction is far more sensitive to light. That the velocity coefficients are practically independent of temperature and proportional to the intensity of incident radiation suggests that the mechanism of reaction may be a simple one. The fact that the velocity coefficient passes through a maximum with increase in iodine concentration, whereas the amount of absorbed light steadily increases as the concentration of iodine increases at once indicates that

Einstein's law of the photo-chemical equivalent in its simplest form is not applicable to this reaction. The following calculation indicates the number of molecules transformed by one quantum of light under different experimental conditions. Radiant energy from a Hefner lamp at a distance of 1 metre whose intensity is equal to 900 ergs per square per cm. sec. produced a galvanometer deflection of 138 divisions. The light absorbed by $0.001N$ iodine is equivalent to 17 divisions of the galvanometer. Hence

$$\text{energy absorbed} = \frac{17 \times 900}{138} \text{ ergs.}$$

Assuming the mean wave-length of efficient light to be 500 $\mu\mu$, $h\nu$ becomes equal to 3.9×10^{-12} ergs. Therefore the number of quanta in the absorbed light $= 28.4 \times 10^{9}$ quanta.

The change of *allo*-acid in 30 min. (see Table II) in 2/3 c.c. of the solution corresponding to a surface of 2/3 sq. cm. $= 6.38$ c.c. of $0.003665 N$ alkali.

Therefore the number of molecules transformed per sq. cm. of surface × thickness of 1 cm. per sec.

$$= \frac{6.38 \times .003665 \times 3 \times 6.16 \times 10^{23}}{30 \times 60 \times 1000 \times 2} = 12 \times 10^{15}$$

Therefore, the number of molecules divided by the number of quanta $= 4.23 \times 10^{2}$.

Results of the same order were obtained with different concentrations of iodine.

It rarely happens that the velocity coefficients pass through a maximum as the concentration of photocatalyst increases. This peculiarity of the solvent action of methyl alcohol was also noticed by Soulan in the relative change in the conductivity of a fluorescent

solution of esculine on illumination. Here too, for the same intensity of illumination, the relative change in the conductivity passes through a maximum as the concentration of esculine in methyl alcohol increases (*vide* Rule, *Phil. Mag.*, 1926, *1*, 538). Similar phenomena are observed in the production of phosphorescence where the intensity of phosphorescence passes through a maximum as the concentration of the active substance in the solid solution increases (Merrit, *Physical Review*, 1915, *5*, 319). Recently Rule (*loc. cit.*) has also observed a similar maximum in the curve representing the variation of the E. M. F. of a photo-active cell prepared from a solution of a fluorescent dye, with the concentration of that dye. Perrin (*Compt. rend.* 1923, *177*, 469) has shown that if the concentration of a fluorescent solution is increased, beginning at zero, the fluorescence begins to incrrese, passes through a maximum and then decreases as the concentration is further increased.

The Elementary Phenomenon of Photo-catalysis by Iodine.

The photo-catalyst molecule of iodine absorbs a quantum of radiation and passes into the excited state. It might revert (1) to the normal stable condition by re-emitting the above quantum of radiation, (2) to another stable condition by emitting a quantum of different radiation, which we call fluorescent radiation, or it might revert to its normal state by colliding with a molecule of *allo*-acid and communicating in that process, its energy of excitation to the *allo*-acid molecules which in their turn under the impulse of this increased energy, become ultimately transformed into the normal acid molecules. The rate of transformation will therefore

be proportional to the concentration of the active iodine molecules and the molecules of the *allo*-acid. The monomolecular velocity constant with respect to *allo*-acid is therefore a measure of the concentration of active iodine molecules under the conditions of experiment. Now Perrin assumes (*Compt. rend.*, 1924, *178*, 1978) that in strong solutions the molecules of the fluorescent body are protected by each other and he suggests the following mechanism (*vide* Rule, *loc. cit.*).

As the concentration increases the amount of light absorbed increases, and hence the number of molecules activated increases until a concentration is reached, when the whole of the effective incident radiation is absorbed. Beyond this point the number of activated molecules cannot increase and should have a constant value but for the protective action of one molecule on another. It may be supposed that a molecule, capable of being brought to an excited condition by the absorption of radiation, takes a certain finite time to attain its new configuration. Now if during this time a second molecule of the same nature approaches near the first, it can acquire, by resonance, part of the energy of the first and so disturb its excited condition. When the solution is dilute the protective action of the molecules over each other is small as the mean distance between the molecules is large; but with increase in concentration the mean distance diminishes and this protective influence plays a more and more important part until the point is reached, where the increase in the number of active molecules due to the mere fact of increase in concentration and hence absorption of light, is compensated for by the reduction in the number of molecules in the requisite excited state due to this protective influence. Beyond this point the reduction in the number of molecules on account of the protective influence is increasingly greater than the

increase in the number of active molecules resulting in increased absorption of light. The maximum point on the velocity constant—iodine concentration curve and the subsequent falling off in the value of the velocity constant are thus explained.

Halogenation. Part I. Iodination.

By

Phuldeo Sahay Varma and Dattatreya Anant Kulkarni.

.Direct iodination of hydrocarbons, aliphatic or aromatic; has always been a matter of difficulty. This difficulty is attributed to hydriodic acid, produced in the course of the reaction, which reduces the iodo-compound as soon as it is formed. It was suggested that the presence of iodic acid would avoid this difficulty by oxidising the hydriodic acid. Some iodo-compounds have been obtained in this way. Attempts have also been made to bring about direct iodination in presence of other substances. Istrati (*Bull. Soc. chim.*, 1891, (3) 5, 158; *Abs.*, 1891, 60, 1197) prepared di-iodobenzene by the action of a mixture of benzene, iodine and sulphuric acid (d 1·84). An iodobenzene sulphonic acid is formed which, along with hydriodic acid, yields sulphur dioxide, water and di-iodobenzene.

$$(i) \quad C_6H_5SO_3H + I_2 = C_6H_4I\cdot SO_3H + HI$$

$$(ii) \quad C_6H_4I\cdot SO_3H + HI = C_6H_4I_2 + SO_2 + H_2O$$
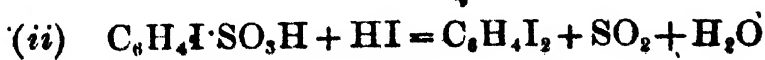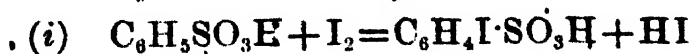
Zernoff (*J. Russ. Phys. Chem. Soc.*, 1900, *32*, 804) carried out a series of experiments on iodination by means of the chloride and bromide of iodine. Körner and Belasio *(Atti. R. Accad. Lincei*, 1908, (V) *17, ii,* 679) iodinated *m*-nitraniline by means of iodine and potassium iodate. Elbs and Jaroslavzev (*J. pr. Chem.*, 1913, (ii) *88,* 92) found that iodo-derivatives of aromatic hydrocarbons could be obtained by boiling the latter with iodine and sodium persulphate in glacial acetic acid solution.

Datta and Chatterji (*J. Amer. Chem. Soc.*, 1917, *39,* 435) succeeded in introducing iodine directly into aromatic hydrocarbons in presence of nitric acid, and obtained good yields of certain iodo-compounds. We find that when nitro-sulphonic acid is added to the mixture of iodine and fuming nitric acid used by Datta and Chatterji, the process takes a shorter time and the yield is improved. The yield is still better if glacial acetic acid is added

Datta and Chatterji explain the reaction by assuming that nitric acid acts not merely as a catalyst but by oxidising the hydrogen of the hydrocarbon, the nitric acid itself being reduced to lower oxides of nitrogen. According to them the view that the nitro compound is first formed and that the nitro group is then replaced by iodine is untenable: they could not obtain even a trace of iodo-benzene from nitrobenzene by digesting it with iodine for a considerable length of time.

Since a mixture of fuming nitric and nitro-sulphonic acid has been found to be a better nitrating agent than the fuming nitric acid alone (Varma and Kulkarni, *J. Amer. Chem. Soc.*, 1925, *47,* 143) we are inclined to the view that the intermediate formation of the nitro compounds does take place before iodine is introduced into the benzene nucleus. It is the presence of this nascent nitrobenzene that helps the

introduction of iodine into the benzene nucleus. The only proof of this assumption is that a small of nitro-benzene is perceived when a few. c.c. of the nitro-sulphonic acid mixture are added to the reacting mixture, whilst no appreciable quantity of nitrobenzene is found in the end products when iodine in sufficient quantity to form iodo-benzene is present there. The reaction may take place according to the equations,

(1) $\quad C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$

(2) $\quad C_6H_5NO_2 + I = C_6H_5I + NO_2,$
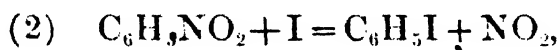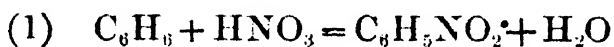
—the nitrogen peroxide passing out of the sphere of reaction. Evolution of brown oxides of nitrogen was observed when nitric acid alone or the nitro-sulphonic acid mixture was used. The action of acetic acid in increasing the yield of the iodo-compounds can be explained by assuming that it helps the reaction by dissolving iodine.

In order to compare the results obtained by the special method adopted in this paper with those obtained by Datta and Chatterji's method, their experiments with slight modifications have been repeated side by side. It is to be noted that the yield by the method of Datta and Chatterji is improved by the mere addition of gla-cial acetic, acid at the outset of the reaction.

EXPERIMENTAL.

The fuming nitric and nitro-sulphonic acid mixture.

This mixture is prepared by passing a steady current of sulphur dioxide into cold fuming nitric acid of specific

gravity 1·5, until about 50 per cent. of nitro-sulphonic acid is obtained. If the percentage of nitro-sulphonic acid in the mixture is greater than 50 it can be brought down to this value by adding to it the required quantity of fuming nitric acid. A mixture thus prepared was used in the following experiments.

Preparation of Iodobenzene.

1. Benzene (30 c. c.) and finely powdered iodine (25 g.) were put into a clean dry flask fitted with a reflux condenser and kept on a water-bath. To this was added the nitro-sulphonic acid mixture (12 c. c.) in portions of 2 c. c. at a time at intervals of 15 minutes. After the whole of the mixture was added the flask was kept on the water-bath for half an hour; the mixture was then allowed to cool and was treated with very dilute sodium hydroxide solution to remove the unchanged iodine, and washed with water. The heavy liquid was then separated, dehydrated with fused calcium chloride and distilled. The portion distilling at 185-88° was collected separately and was found to be iodobenzene. Yield 15·6 g.

2. Experiment No. 1 was repeated with the addition of glacial acetic acid (3 c. c.) at the beginning of the experiment. The yield of iodobenzene increased to 23·0 g.

3. Experiment No. 1 was repeated using concentrated nitric acid (sp. gr. 1·42) instead of the mixture of fuming nitric and nitro-sulphonic acid. The yield of iodobenzene was 12·5 g. (the experiment of Datta and Chatterji with slight modifications).

4. Experiment No. 3 was repeated with the addition of glacial acetic acid (3 c. c.). The yield of iodobenzene was 17·8 g.

5. A number of experiments have been carried out with the object of finding the proportions that produce the maximum yield of iodobenzene. The results obtained are recorded in the table below:—

Expt.	Benzene.	Iodine.	Acetic acid.	Nitro-sulphonic mixture.	Iodobenzene.
a	30 c. c.	25 g.	Nil.	Nil.	Nil.
			3 c. c.	5 c. c.	14·0 g.
			,,	7 ,,	17· 0
			,,	9 ,,	19·5
			,,	12 ,,	23·0
			,,	15 ,,	22·5
			,,	18 ,,	22·0
			,,	25 ,,	20·0

Preparation of Iodotoluenes.

6. Toluene (30 c. c.), iodine (25 g.) and glacial acetic acid (8 c. c.) were mixed. The nitro-sulphonic acid mixture (12 c. c.) was added gradually and the whole process was carried out as in Experiment 1. The liquid product (washed and dried) was distilled, and the fraction distilling between 209 and 212° was collected

separately and was found to be a mixture of *ortho-* and *para-*iodotolueness. Yield 21·5 g. A small residue was left in the distilling flask.

7. Experiment No. 6 was repeated using concentrated nitric acid (sp. gr. 1·42). The yield of the two iodotoluenes was found to be 13·5 g.

Simultaneous Adsorption of Ions from Solution. Part I. Adsorption of Metal Ions by Hydrated Manganese Dioxide.

BY

MOOLRAJ MEHROTRA AND KSHITISH CHANDRA SEN.

A certain amount of work has been done on the simultaneous adsorption of two solutes from solution by adsorbents. Thus Masius ("Uber die Adsorption in Gemischen," *Dissertation*, Leipzig, 1908) studied the simultaneous adsorption of mixtures of organic acids by blood charcoal and arrived at the conclusion that less of each was adsorbed than if the other was not present. A similar result was also obtained by Freundlich and Poser (*Kolloid-Chem.* Beih. 1914, *6*, 499) with mixtures of organic acids and alumina. Schmidt (*Zeit. physikal. Chem.*, 1910, *74*, 730) also found a similar result in the adsorption of iodine and acetic acid by charcoal. Other works in this line are those of Lachs and Michaelis (*Zeit. Elektrochem.*, 1911, *17*, 1), Freundlich and Kaempfer (*Zeit. physikal. Chem.*, 1915, *90*, 681), Rona and Michaelis (*Biochem. Zeit.*, 1909, *16*, 499); Bancroft ("Applied Colloid Chemistry", 1921, 113) has summarised the main work in this direction.

The work described in this paper was undertaken to throw some light on the phenomenon of antagonistic action of ions in the coagulation of colloids, specially in relation to the so-called displacement of adsorption of one ion in the presence of another adsorbable ion of the same charge, a point on which Weiser (*J. Phys. Chem.*, 1921, *25*, 399; 1924, *28*, 232) in some recent papers has

laid much stress. According to him the antagonistic action of two electrolytes is, in the main, due to the fact that the presence of one coagulating ion in some cases cuts down the adsorption of the other and hence stabilises the sol towards that coagulating ion. It was, however, shown by one of us (cf. Sen, *J. Phys. Chem.*, 1925, 29, 536) that this fact alone would not be enough to cause the antagonistic action. Though the adsorption of each is separately diminished, the total adsorption of both the ions may be equivalent to the adsorption of either of coagulating ions when only one is present at the coagulating concentration. Since the coagulation of a colloid depends primarily upon a decrease in the effective charge on the colloid particles, equivalent amounts of different ions are necessary for it. Hence when the sum total of the adsorption of the ions separately expressed in electro-chemical equivalents reaches a certain limit, the colloid will be coagulated irrespective of whether the original point of adsorption of one ion when present alone to coagulate the sol has been reached or not. In order to support the explanation of Weiser it is necessary to show that though one of the ions is not appreciably adsorbed, simply by its presence the adsorption of a second ion is diminished considerably. This effect would then be similar to the so-called "poisoning" of catalysts. It was felt that the existing data on adsorption including those of Weiser are inadequate for a proper study of this subject because in no case a simultaneous measurement of the adsorption of both the coagulating ions has been made. Thus Weiser (*loc. cit.*), in the coagulation of arsenious sulphide sol by a mixture of lithium and barium salts, observed that the adsorption of barium ion is cut down by the presence of lithium but he did not determine the amount of adsorption of the lithium ion at the same time.

In this paper we have given the results of the simultaneous adsorption of several metallic ion pairs by hydrated manganese dioxide. We have used a precipitated sample instead of a sol because it has been found that the precipitated oxide can be obtained in a much purer state than the colloid and secondly, the results in both the cases are similar, varying only in the absolute amount of adsorption.

EXPERIMENTAL.

The hydrated manganese dioxide was prepared by the Volhard's reaction in presence of strong potassium nitrate solution, washed free from electrolytes and then air dried. Two grams of the same preparation have been used in each experiment, the total volume of the solution being always 50 c.c. The mixtures examined are $BaCl_2 + CuCl_2$, $Ba(NO_3)_2 + AgNO_3$, $Ba(NO_3)_2 + KNO_3$, $Ba(NO_3)_2 + Al(NO_3)_3$, and $AgNO_3 + KNO_3$. Copper was estimated volumetrically by means of thiosulphate, and silver, by means of thiocyanate; barium and potassium gravimetrically as sulphates and aluminium as oxide. The time allowed for adsorption to take place was twenty hours though it was found that equilibrium was reached much earlier.

TABLE I.

Adsorption of Copper from $CuCl_2 + BaCl_2$.

Original concentration of Cu in milli-equivalents.	Adsorption of Cu in milli-equivalents.			
	$Ba = 0$	$Ba = 1$ milli-equivalent.	$Ba = 15$ milli-equivalent.	$Ba = 20$ milli-equivalent.
24·32	2·42	1·92	...	...
18·24	2·24	1·89	1·79	1·64
12·16	1·96	1·76	1·56	1·26
6·08	1·65	1·48	1·33	1·08

TABLE II.

Adsorption of Ba·· *from* $BaCl_2 + CuCl_2$.

Original concentration of Ba·· in milli-equivalents	Adsorption of Ba·· in milli-equivalents.				
	Cu··=0	Cu··=6·08 milli-equivalent.	Cu··=12·16 milli-equivalent	Cu··=18·24 milli-equivalent.	Cu··=24·32 milli-equivalent.
20	1·366	1·238	1·058	0·955	...
15	1·255	...	...	0·724	...
10	1·109	0·865	0·724	0·659	0·484
5	0·827	...	...	...	

TABLE III.

Adsorption of Ag· *from* $AgNO_3 + Ba(NO_3)_2$.
and $AgNO_3 + KNO_3$.

Original concentration of Ag· in grams.	Adsorption of Ag· in grams.				
	Ba··=0 K·=0	Ba··=0·3434 gm.	Ba··=1·0363 gm.	K·=0·391 gm.	K·=0·5865 gm.
2·1596	0·4413	0·4413	...	...	...
1·6197	0·3922	0·3922	...	...	0·3922
1·0798	0·3360	0·3360	0·3360	0·3360	...
0·5399	0·2581	0·2581	0·2574	...	...

TABLE IV.

Adsorption of Ba·· from $Ba(NO_3)_2 + KNO_3$
$Ba(NO_3)_2 + Al(NO_3)_3.$

Original concentration of Ba·· in milli-equivalents.	Adsorption of Ba·· in milli-equivalents.			
	$K· = 0$ $Al··· = 0$	$K· = 10$ milli-equivalent.	$K· = 15$ milli-equivalent.	$Al··· = 14·61$ milli-equivalent.
20	1·43	...	...	...
15	1·40	...	0·92	1·32
10	1·126	0·99	..	...
5	0·952	...	...	

TABLE V.

Adsorption of Al··· from $Al(NO_3)_3 + Ba(NO_3)_2.$

Original concentration of Al··· in milli-equivalents.	Adsorption of Al··· in milli-equivalents.	
	$Ba·· = 0$	$Ba·· = 15$ milli-equivalent.
14·61	1·44	1·027

TABLE VI.

Adsorption of K· from $KNO_3 + Ba(NO_3)_2.$

Original concentration of K· in milli-equivalents.	Adsorption of K· in milli-equivalents.	
	$Ba·· = 0$	$Ba·· = 10$ milli-equivalent.
40	0·39	0·17

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Discussion.

It will be observed from the above tables that with the exception of silver nitrate the adsorption of other metallic ions such as copper, barium, potassium and aluminium is decreased in presence of another adsorbable ion. These results are therefore in line with the results of other workers already mentioned. Thus with increasing concentration of either copper or barium in a solution containing a given amount of the other the adsorption of each is more and more diminished. The results are plotted in Figs. I and II. The case of silver, however, appears to be an interesting one and it seems probable that the adsorption complex of silver and manganese dioxide is a more stable one than others. Recently Pawlow (*Kolloid. Zeit.*, 1924, 35, 375) has suggested that the adsorption of silver by manganese dioxide is a case of complicated chemical adsorption where silver reacts with $Mn(OH)_4$ yielding various salts of the type, $Mn(OH)_3,AgO$, $Mn(OH)_2$, $(AgO)_2$ etc., resulting in the liberation of free acid. It may be stated here that silver, though a monovalent ion, has a very high precipitating power on a manganese dioxide sol and it has been found in general that ions which have a great chemical affinity for a colloid usually possess a great precipitating power. The difference between the behaviour of silver and barium seems therefore to point that in the adsorption of silver the adsorptive forces approach more nearly those of primary valency forces.

Patrick and Barclay (*J. Phys. Chem.*, 1925, 29, 1400) have found that in the replacement of alkali by means of silver, copper, and ferric ions on a silica surface, equivalent amounts of sodium are replaced by each of the heavier ions. From our tables, however, it will be
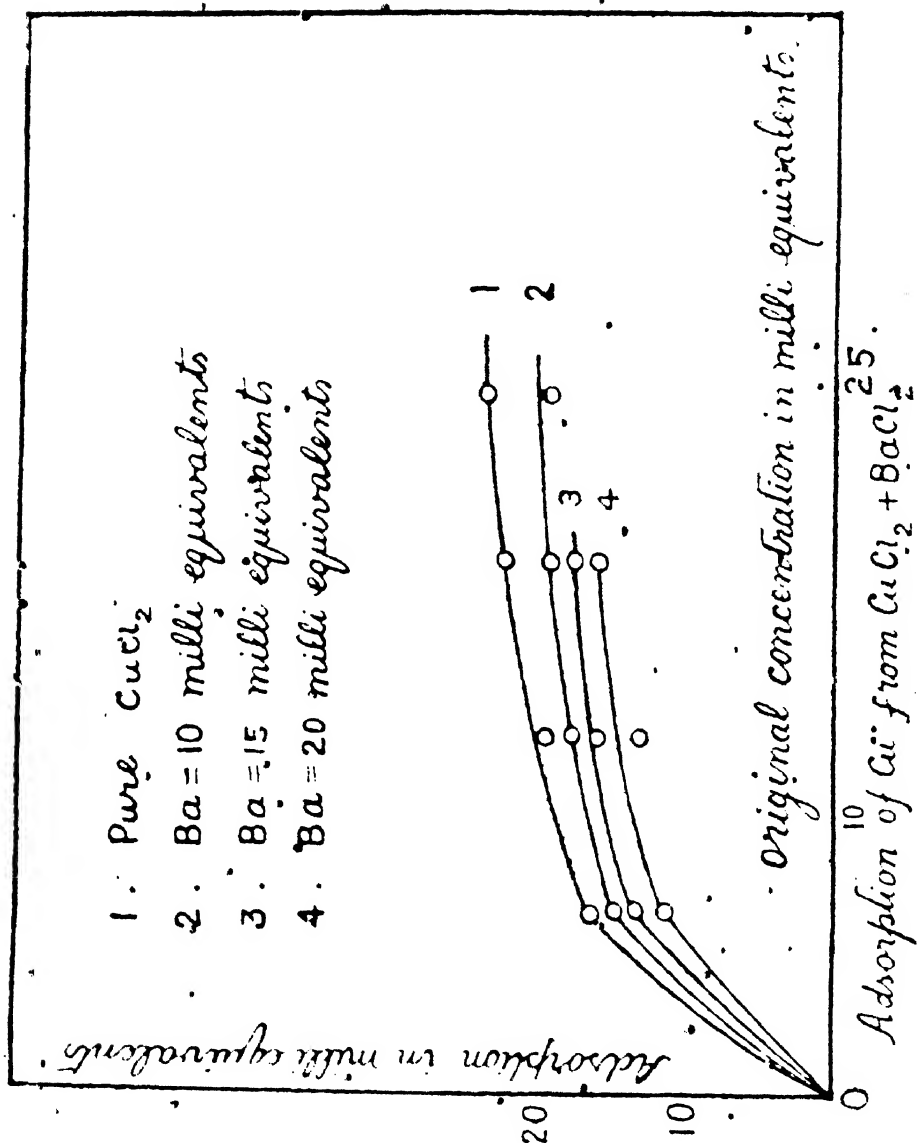
FIG. I.
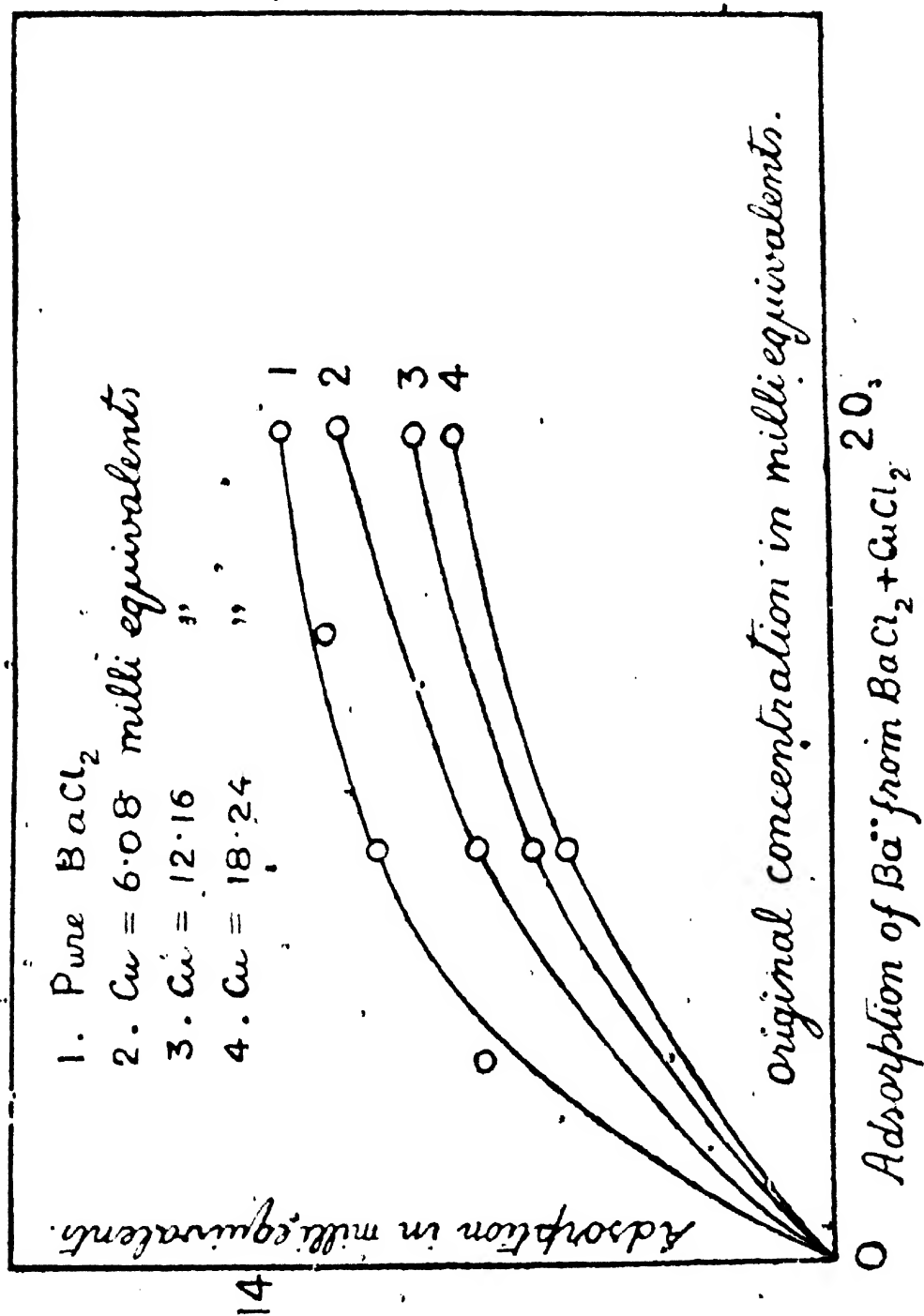
FIG. II.

apparent that the amount of adsorbed ion is never equivalent to the adsorption of the replaced ion. On the other hand the sum of the adsorption of two ions expressed in equivalents is always greater than the amount of adsorption of either of them at the same concentration when only one is present. Further, in the mixture potassium nitrate and barium nitrate it will be observed that though the adsorption of barium is decreased considerably in presence of potassium, yet at the same time the combined adsorption of potassium and barium is greater than either that of potassium or barium when each is present alone. Should this result be confirmed in the case of arsenious sulphide sol then we think that Weiser's explanation regarding the antagonistic action of potassium and barium ions remains no longer valid.* In Table VII the results of two experiments of this nature are summarised.

TABLE VII.

Cation	Original concentration in milli equivalent.	Adsorption separately.	Adsorption from mixture.	Sum.	Percentage decrease.
Ba··	10	1·126	0·99	} 1·16	12
K·	10	0·39	0·17		30
Ba··	10	1·109	0·724	} 2·484	38
Cu··	12·16	1·96	1·76		9·9

* We may state here also that though potassium ion cuts down the adsorption of barium yet there is no antagonistic effect between these two salts in the case of manganese dioxide colloid. Hence simply the cutting down of the adsorption of one cation by another cannot be a sufficient explanation or a proof of the existence of cationic antagonism with As_2S_3 sol.

· Another point of interest in Table VII is the percentage decrease of adsorption of one ion in the presence of another. Thus barium is much more adsorbed than potassium and along with it the decrease in the amount of adsorption of barium in presence of potassium is about twelve per cent., whereas under the same conditions the adsorption of potassium ion is decreased to the extent of about thirty per cent. In the case of the mixture, copper and barium, copper is much more adsorbed than barium and the percentage of the replacement of copper by barium is also much less than that of barium by copper. These results therefore support the general observation of many workers that the more adsorbable ions are less readily replacable.

Mention may be made here of another fact which at first appeared to be puzzling. Thus in the adsorption of barium from a mixture of barium chloride and a low concentration aluminium nitrate, it was found that instead of decreasing, the adsorption actually increased to more than that from pure barium chloride. It was found out, however, that the presence of nitrate ion increases the amount of adsorption of barium ion by manganese dioxide. Similarly in presence of sulphate, adsorption of copper is increased from a solution of copper chloride. In Tables VIII and IX these data are shown. It will be observed that the anion has a very marked effect on the adsorption of the cation.

TABLE VIII.

Adsorption of Ba·· *from* Ba(NO₃)₂ *and* BaCl₂.

Original concentration of Ba·· in milli-equivalents.	Adsorption of Ba·· in milli-equivalents.	
	Adsorption from BaCl₂	Adsorption from Ba(NO₃)₂.
20	1·366	1·43
15	1·255	1·40
10	1·109	1·126
5	0·827	0·952

TABLE IX.

Adsorption of Copper from CuSO₄ *and* CuCl₂.

Original concentration of CuSO₄ in milli-equivalents.	Adsorption of Cu·· in milli-equivalents.	Original concentration of CuCl₂ in milli-equivalents.	Adsorption of Cu·· in milli-equivalents.
25·5	3·20	24·32	2·42
20·4	3·14	18·24	2·24
15·3	2·88	12·16	1·96
10·2	2·54	6·08	1·65
5·1	1·99		

The reason for this behaviour is that sulphate ion has been found to be more adsorbed than chloride in the case of copper salts (*Cf.* Sen, *Biochem. Zeit.*, 1926, *169*, 192). It appears probable that nitrate ion is also more adsorbed than chloride in the case of barium salts. This result is thus similar to that of Weiser (*J. Phys. Chem.*, 1926, *30*, 27), who has recently found that barium is more adsorbed from barium ferrocyanide than from barium chloride by arsenious sulphide sol. Bancroft (*loc. cit.*) also cites

references about the effect of acid and alkali in increasing the amount of adsorption of acidic and basic dyes respectively.

In conclusion we may state that experiments are now in progress on the simultaneous adsorption of ions by arsenious sulphide, ferric hydroxide and aluminium hydroxide sols and also the coagulation of these sols and that of manganese dioxide by the same mixtures of electrolytes and hence a theoretical discussion on the relation between these two phenomena is postponed for the next communication.

Summary.

1.   An experimental study has been made of the simultaneous adsorption of several pairs of metallic ions by hydrated manganese dioxide.

2.   It has been found that the adsorbed silver cannot be replaced by either potassium or barium. Both potassium and barium can, however, be displaced one by the other. Copper and aluminium are also displaced by barium and *vice versa.*

3.   In general, with increasing concentration of the replacing ion in solution more and more of the adsorbed ion is displaced.

4.   It has been found that the ion which is more adsorbed is less readily replaced by a less adsorbable ion.

5.   The cation is more adsorbed from a salt which contains a highly adsorbable anion.

6.   The sum of the adsorption of two ions from a mixture is always greater than the adsorption of either of them when present alone in the solution.

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Experiments on Charge Reversal by Hydrogen and Hydroxyl Ions with insoluble Organic Acids and Amines and Reversal of the Charge of Hydrated Silica and Copper Oxide by Solutions of Salts.

BY

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The influence of hydrogen and hydroxyl ions on the charge of colloidal particles is in some respects distinct from that of other ions. Firstly, their capacity to decrease the electrical charge of a colloidal surface of opposite sign is, in general, greater than that of other ions of the same valency. Secondly, reversal of the sign in the initial charge is to be met with more frequently in literature, when the colloid is brought in contact with acids or alkalis. Attention has been drawn to this peculiar behaviour of hydrogen and hydroxyl ions by Perrin (*J. Chim. Phys.*, 1904, 2, 601), Haber and Klemensiewicz (*Z. physikal. Chem.*, 1909, 47, 385) and others. One of us has reviewed the subject (*Phil. Mag.*, 1922, 44, 322) and pointed out the defects in the explanation of Perrin. Haber assumed that the surface, in virtue of its hydration, acts as a hydrogen and oxygen electrode. It

is well known that 'electrode' potentials are not identical with what has been termed by Freundlich as 'electrokinetic' potentials. The behaviour of hydrogen and hydroxyl ions was explained in the last mentioned paper from the point of view of the adsorption of ions and from considerations of neutralisation of hydrogen and hydroxyl ions in the fixed layer of water molecules on the surface, by hydroxyl and hydrogen ions respectively present in the solution (*loc. cit.*). Recently Bartell and Miller (*J. Amer. Chem. Soc.*, 1922, 44, 1826; *ibid*, 1923, 45, 1106) have made the very interesting observation that specially prepared charcoal, uncontaminated by any kind of inorganic salts, acids or alkalis when brought into contact with neutral solutions of salts, can give rise to acid or alkali. These authors (*J. Phys. Chem.*, 1924, 28, 992) in explaining this so called hydrolytic adsorption points out that it is necessary to make assumptions similar to what has been suggested by Mukherjee.

Fajans (*Z. Physical. Chem.*, 1921, 97, 478) and Mukherjee (*Far. Soc.* Disc., Oct., 1920) have pointed out that a strong adsorption of constituent ions by polar precipitates is to be expected (*vide* also Mukherjee and Roy, *J. Indian Chem. Soc.*, 1924, 1, 173 ; Taylor, *J. Phys. Chem.*, 1925, 29, 942). It is therefore of interest to see whether hydrogen and hydroxyl ions could not behave in a similar manner with insoluble acids and bases, For this purpose we undertook an examination of the effect of hydrogen and hydroxyl ions on the charge on the surfaces of particles of insoluble organic acids and amines. It would be also of interest to see which of the above two explanations will represent the facts better in such cases. In the course of this investigation, we have come across a fact of considerable interest regarding the theory of adsorption of ions. We have found that contrary to general

experience, in a number of cases, the charge on these particles as measured by the rate of electro-osmosis, is not affected by multivalent ions of opposite sign, though hydrogen and hydroxyl ions have a characteristic effect.

EXPERIMENTAL.

The variations in charge were measured by electro-osmotic experiments. The arrangement we used is that described in *Nature*, Dec. 2, 1922 (see also Mukherjee and B. C. Roy, *J. Chem. Soc.*, 1924, *125*, 480). The results recorded in this paper are of a semi-quantitative nature. Provided the movement of the air bubble is not too small, they are reproducible within 5 per cent.

In these experiments care was taken to see that the conditions were as far as possible identical. To minimise variations in temperature, the apparatus was immersed in a large bath of water. After each reading the substance in the bent portion of the U-tube was left at rest for some time.

.. The various sparingly soluble organic acids, which were used as diaphragms, were all recrystallised from absolute alcohol and washed thoroughly with conductivity water. The same sample was used for all the experiments. The substance was carefully washed with the electrolyte in question in steamed Jena-glass bottles and then kept in contact with the electrolyte for 24 hours, after which they were used for the electro-osmotic experiments.

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TABLE I (A)*.

Sparingly soluble Acids.

——

Electrolyte : *Hydrochloric Acid*.

Concentration of electrolyte.	Benzoic acid.	Cinnamic acid.	Salicylic acid.	Boric acid.
Pure Water.	+ 1·4	− 10·6	− 8·1	− 3·2
N 5000	+ 2·5	− 9·5	...	
N/2000	...	..	...	− 2·7
N/1000	+ 4·5	− 52	− 0·4	..
N/500	+ 0·8	− 1·3	− 0·2	− 0·5
N/100	0·0	− 0·6	0·0	+ 1·25

TABLE I (B).

Sparingly soluble Acids.

Electrolyte : *Sodium Hydroxide*.

Concentration of electrolyte.	Benzoic acid.	Cinnamic acid.	Salicylic acid.	Boric acid
Pure water value.	+ 1·4	− 10·6	− 8·1	− 3·2
N/5000	+ 0·7	..	− 11·3	:.
N/2000	0·25	− 9·0	...	− 3·5
N/1000	...	− 16·0	− 13·7	...
N/500	0·0	− 18·6	− 12·4	− 4·0
N/250	...	− 21·9	...	...
N/100	− 2·85	− 18·6	− 10·0	− 8·35

* The electro-osmotic data given above represents the distance in cms. moved by the air bubble in 3 minutes. The sign in this and following tables indicates the sign of charge of the particles.

TABLE II (A).

Sparingly soluble Amino acids.

Electrolyte : *Hydrochloric Acid.*

Concentration of electrolyte.	Phenyl-glycine-o-carboxylic acid.	m-Amino-benzoic acid.
Pure water	−1·2	+0·35
N/5000	−0·9	+1·1
N/1000	+1·8	+4·5
N/500	+2·4	+6·6
N/250	+2·9	+8·9
N/100	+4·6	+12·0

TABLE II (B).

Sparingly soluble Amino-acids.

Electrolyte : *Sodium Hydroxide.*

Concentration of electrolyte,	Phenyl glycine-o-carboxylic acid.	m-Amino-benzoic acid.
N/5000	−1·45	−0·5
N/2000	−1·60	−1·35
N/500	−1·65	−1·85
N/250	−1·60	−5·60
N/100	−1·60	−8·50

TABLE III.

Sparingly soluble Amine dnd Ester.

Concentration of electrolyte.	p-Nitraniline.	Salol.
Pure water value	−15·70	−19·5
Hydrochloric acid		
N/2000 ...	−7·35	−12·7
N/500 ...	−2·70	−8·2
N/100 ...	+3·0	−5·1
Sodium Hydroxide		
N/2000 ...	−18·5	−30·0
N/500 ...	−18·0	−32·2
N/100 ...	−13·5	−30·0

TABLE IV.

Electrolyte : *Potassinm Chloride*

Concentration of electrolyte.	Boric acid.	Benzoic acid.	Cinnamic acid	Salicylic acid.
Pure water ...	−3·2	+1·4	−8·0	−8·1
N/5000 ...	−1·9	+1·5	−8·3	−7·3
N/1000 ...	−1·9	...	−8·3	−7·3
N/500 ...	...	+1·4	−8·2	−7·5
N/100 ...	−0·4	+1·3	−8·2	−8·0

TABLE V.

Electrolyte : *Barium Chloride.*

Concentration of electrolyte.	Boric acid.	Cinnamic acid.
N/5000	−1·95	−9·0
N/1000	−1·90	−9·0
N/500	−1·90	−9·5
N/100	−0·70	−9·0

TABLE VI.

Cinnamic Acid and Aluminiun Chloride.

Concentration of aluminium chloride.	Charge.
0	−8·0
N/2000	−7·02
N/500	−1·2
N/100	0·0

Electro-osmotic experiments were also carried out with one inorganic insoluble acid and one insoluble base, namely hydrated silica and hydrated copper oxide. Only two electrolytes were used for experiments with silica as a number of electrolytes have been previously examined in this laboratory.

TABLE VII.

Hydrated Silica.

Concentration of electrolyte	Aluminium chloride.	Aniline hydrochloride.
Pure water value.	−3·5	−3·5
N/10,000	...	−3·6
N/5,000	−4·6	−2·3
N/2,500	−4·2	−1·0
N/1,000	−2·4	−0·1
N/500	+0·5	+0·45
N/250	+1·6	+1·10
N/100	+1·5	+2·0

TABLE VIII.

Hydrated Copper Oxide.

Concentration of electrolyte.	Potassium sulphate.	Potassium chloride.	Sodium chloride.	Barium chloride.	Potassium nitrate.	Rubidium nitrate.
Pure water value	+2·757*	+4·4	+4·4	+4·4	+4·25	+4·25
N/5,000	+7·0	+11·6 (?)	+13·7	...	+14·7	+14·6
N/1,000	+4·0	+16·5	+15·4	+14·9	+16·0	+12·7(?)
N/500	+2·6	+14·7	+14·3	+14·2	+13·6	+14·9
N/250	+1·6	...	...	...	...	...
N/100	−1·6	+13·3	+13·5	+13·6	+12·6	+13·1

* A different sample of the hydrated copper oxide was used for this experiment

DISCUSSION.

(A). *Adsorption of Constituent Ions.*

We shall consider in this section the influence of alkalis and acids on the charge on the insoluble organic acids, bases, and also on salol. From Tables I to III, it is evident that while benzoic and *m*-aminobenzoic acid are positively charged in contact with their own solution in pure water, the other acids investigated are negatively charged It is to be noted that the positive charge on the particles is markedly increased or negative charge diminished by hydrochloric acid. In the case of boric and the amino acids we actually notice a reversal of charge. Boric acid behaves in one sense differently from the other acids. Alkali has little effect on its charge. It is probable that on account of the solubility of the acid and the greater strength of adsorption of the anion, the surface is nearly saturated with anions when the substance is in contact with its own saturated solution. In the other cases investigated, *e.g.*, salicylic and cinnamic acid in presence of hydrochloric acid, the charge tends to a zero value but up to the concentration used no reversal has been observed. In those cases where the particles have initially a small negative charge, it seems that a reversal can be observed whereas with cinnamic and salicylic acid there is no reversal of charge probably on account of the initial high negative charge on the surface. We could not use higher concentrations of acid, as the evolution of gases on account of electrolysis produces a serious source of error in our measurements. In fact, the change in volume consequent on evolution of gases is already a source of error at the higher concentrations for which measurements are given in the tables. Further it should be noted that the figures given above can give us no

definite information regarding the relative intensities of the adsorption by these substances as the size of the capillary passages, the actual potential drop and the potential gradient are not all identical. The values, however, give us a qualitative idea of the general nature of the variations.

Regarding the influence of the hydroxyl ion on the charge on these surfaces, it is noticed that in all these cases, with two exceptions, the particles become more negatively charged. In the alkaline solutions there are evidently the anions of these acids, *i.e.*, benzoate, cinnamate, salicylate, etc., and the results obtained show that there is a strong tendency towards the adsorption of these constituent ions. Even in this case, we notice that at a higer concentration there is a slight but much less marked diminution of the negative charge which again points to the electrical adsorption of the cation.

In the case of the two amino acids which are amphoteric, we notice a greater tendency on their part to get positively charged. It is also to be observed that the increase in the negative charge on the addition of alkali is not so great as for the other acids. The presence of amino group seems to increase the adsorption of the hydrogen ions and decrease that of the anion or hydroxyl ions.

To sum up, we notice :

(a) For the acids, a strong adsorption of constituent ions.

(b) In the contact with saturated solution of the acids, two of them (benzoic acid and m-aminobenzoic acid) are positively charged. The rest are negatively charged. It seems that of the constituent ions, in some cases, the hydrogen and in other case the anion (or hydroxylion) is more strongly adsorbed.

(c) At higher concentrations the adsorption of the ion with a charge of opposite sign to that carried by the surface becomes more pronounced.

(d) The amino acids take up a positive charge more easily than the others implying that the amino groups on the surface react with hydrogen ions in solution and lead to the adsorption of the latter. The strength of the adsorption of the hydrogen ions is also indicated by the fact that even at fairly high concentrations, the positive charge does not decrease on account of the anion adsorption. Hydrogen ions are thus more strongly adsorbed than the anion (hydroxyl ions).

(e) It is rather surprising that both p-nitraniline and salol carry a negative charge in contact with pure water, indicating strong adsorption of the hydroxyl ions. A reversal of charge has not been observed for salol up to a concentration of $N/100$ hydrochloric acid. The strong adsorption of the hydroxyl ions is also indicated by the very large increase in the negative charge in the presence of sodium hydroxide. In both these cases we have to conclude that the hydroxyl ions (of the anion of the acid) are more strongly adsorbed than the hydrogen ions.

From the above, it appears that the constitution of the acid has a decided influence on the intensity of adsorption of hydrogen ions and of the anion of the acid, but it is also to be noted that considerations of constitution alone cannot give us an indication of the strength of adsorption of the ions. This is what is to be expected if the adsorption of the constituent ions lead to the growth of the crystal in conformity with its structure. Though the conditions in the interface are not the same as those inside the crystal, yet the energy change associated with the change in hydration, should also be taken into account.

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.We have stated in the introduction that the strong adsorption of the hydrogen ions may be referred either to the adsorption of a constituent ion or to the neutralisation of the hydroxyl ions in the fixed layer of adsorbed water molecules by the hydrogen ions in the solution. The fact that the substances in contact with their saturated solutions are either positively or negatively charged according to their nature points definitely to the primary and preferential adsorption of one of the ions (compare Mukherjee, *Phil. Mag.*, *loc. cit.* p. 330).

(B). *Effect of Solutions of Salts on the Charge of sparingly Soluble Acids.*

It is well known that the adsorption of constituent ions is much more intense than that of other ions, even if they carry a charge of opposite sign to that of the surface. From Tables IV, V and VI we find that neutral electrolytes have very little effect on the charge. In the case of boric acid, we find that both potassium chloride and barium chloride bring down the charge to nearly zero at a concentration of $N/100$; whereas in the case of cinnamic, salicylic and benzoic acids, neutral electrolytes have practically no effect on the charge. On comparing the effect of aluminium chloride with that of hydrochloric acid on cinnamic acid, we find that there is very little difference between the two sets of values. Considering that hydrogen ions are present in the solution on account of hydrolysis, aluminium ions do not seem to have much effect. The observation that potassium and barium chloride and probably aluminium chloride have very little effect on some of the acids is rather unusual. We are not aware of similar observations. The great difference in the adsorption between the ions of neutral electrolytes, and the constituent ions, *points to the*

conclusion that the latter are primarily adsorbed by chemical forces and are not electrically adsorbed in a hydrated state. These observations also point to the conclusion that the surface is strongly hydrated, and consequently the electrical adsorption as defined by one of us is very weak. It has been pointed out by one of us, (*Phil. Mag., loc. cit.*) that adsorption of hydrogen ions or hydroxyl ions from the solution in a dehydrated state cannot be distinguished from the neutralisation by these ions of the hydroxyl or hydrogen ions respectively present in the primarily adsorbed layer resulting from the dissociation of water molecules. The weakness of the adsorption of other oppositely charged ions and the strong effect of hydrogen ions point to the existence of this type of neutralisation. Thus we are inclined to believe that in addition to a strong adsorption of constituent ions, we are dealing with the neutralisation of hydroxyl and hydrogen ions present in the primary layer, by hydrogen and hydroxyl ions respectively in the solution and resulting in the formation of water molecules.

The observation that the charge of boric acid is not at all affected by alkali can be explained from this point of view if we assume that boric acid being a relatively stronger acid, the hydroxyl ion concentration is smaller, and hence the neutralising effect is almost absent. As stated before, the surface must be assumed to be saturated with anions at low concentration.

(C). *Inorganic Acids and Bases.*

It has been observed by Krishnamurti[*] in this laboratory that up to a concentration of $N/100$, hydrochloric acid does not reverse the charge of hydrated silica. He could not also observe a reversal in the charge with

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[*] Unpublished work.

barium chloride. As silica is negatively charged in contact with water it was expected that trivalent ions may reverse the charge. Mukherjee and B. C. Roy (*J. Chem. Soc.*, 1924, *125*, 476) observed that in presence of aniline hydrochloride the negatively charged sols of mastic, gamboge, etc., become positively charged. It will be seen from Table VII that both aluminium chloride and aniline hydrochloride produce a reversal in the charge of silica. The absence of a reversal with acids is probably connected with the fact that the hydrogen ion is not a constituent ion of the solid phase as it is in the case of the organic acids. The silicic acid molecules probably exist on the surface only and there in a hydrated state. The initial rise in the charge followed by a reversal observed with aluminium chloride is of considerable theoretical interest as this form of the curve is difficult to explain from the point of view of the independent adsorption of cations and anions by a negatively charged surface (Mukherjee, *Phil. Mag.*, *loc. cit.* p. 343).

The influence of neutral electrolytes on copper hydroxide is in contrast to their effect on the organic acids or on silica. These results have an important bearing on the nature of the exchange of ions between those in the double layer and those in the solution. It will be seen from Table VIII that sulphate ions can reverse the charge and we attribute this property to its being divalent. The ions in the primary layer must be assumed to be univalent. They are probably cupric ions with a 'fixed' hydroxyl ion forming univalent units. What is more interesting to observe is that all the other five electrolytes practically show the same behaviour and the positive charge increases in each case to a maximum and then decreases. For the chlorides *the rate of flow at the same normal concentration is practically independent of the cation.* The increase in the charge cannot be

due to the adsorption of cations, as otherwise differences between the effect of different cations were sure to have been observed. The increase in the charge probably indicates that the anion of the electrolyte penetrates the double layer, and a redistribution of ions takes place, and a number of hydroxyl ions are displaced from the double layer and that a larger number of positively charged copper ions remain 'uncovered' than before. The ions in the primary layer must be in equilibrium with those in the mobile sheet. The relative numbers of hydroxyl ions and other anions in the mobile sheet are mainly determined by their relative concentrations in the solution. There being now a considerable number of anions (other than hydroxyl) in the mobile sheet, the anions in the primary layer which cover the 'fixed' cupric ions will in part consist of the anions of the electrolyte. On account of the weaker adsorbability of chloride or nitrate ion as compared with that of hydroxyl ions there will remain a larger number of free positive charges in the primary layer.

Summary and Conclusion.

(1) Acids and alkalis have a marked effect on the charge on the surface of particles of insoluble organic acids.

(2) Insoluble organic acids (including amino acids) show a strong adsorption of the constituent ions, and one of the constituent ions is in general more strongly adsorbed than the other.

(3) Neutral electrolytes, e.g., potassium chloride or barium chloride have little effect on the charge of the sparingly soluble acids.

(4) It has been shown that besides a strong adsorption of constituent ions we have evidence of the adsorption of

hydrogen and hydroxyl ions in a dehydrated state. This type of adsorption probably consists in part in the neutralisation of hydrogen and hydroxyl ions in the primary layer (which are formed by the dissociation of fixed water molecules) by hydroxyl and hydrogen ions respectively in the solution.

(5) Presence of the amino group increases the adsorbability of hydrogen ions.

(6) Aniline hydrochloride and aluminium chloride reverse the charge of silica. With aluminium chloride there is an increase in the negative charge at low concentrations and then a decrease followed by a reversal.

(7) Sulphate ions reverse the charge of copper oxide. No reversal has been observed with chloride and nitrate. Neutral electrolytes increase the positive charge of copper hydroxide. The effect depends on the anion and is independent of the nature of the cation (potassium, sodium, barium). The importance of this observation has been pointed out.

Nitration. Part II.* Simultaneous Diazotisation and Nitration of Aromatic Amino-Compounds.

By

Phuldeo Sahay Varma and P. V. Krishnamurthy.

A few cases of simultaneous diazotisation and nitration have been noticed where the active agent used for the purpose was nitrous acid. 2:6-Dinitro-cresol was obtained by treating 2-nitro-p-toluidine with an excess of nitrous acid by Knecht (*Ann·len*, 1882, *215*, 90). 2:6-Dinitro-cresol was produced by the action of nitrous acid on p-toluidine (Martius and Wichelhaus, *Ber.*, 1869, *2*, 207). 5-Brom-3-nitro-cresol was obtained along with brom-o-cresol by the action of nitrous acid on brom-o-toluidine (Claus and Jackson, *J. pr. Chem.*, 1881, (ii), *38*, 32; Wrobleskwi, *Annalen*, 1873, *168*, 165).

A systematic investigation of the subject was carried on by Deninger (*J. pr. Chem.*, 1889, (ii), *40*, 296) who tried the action of nascent nitrous acid (obtained in the reacting mixture by the action of acids on sodium nitrite) on various amino-compounds and obtained nitro-phenolic compounds. He succeeded thus in getting o- and p-nitro-phenols from aniline, o- and p-nitro-cresols from o-toluidine and a nitro-cresol from p-toluidine, dinitro-diphenol and

dinitro-di-cresol from benzidine and toluidine, β-nitro-α-naphthol and dinitro-naphthol from α-naphthylamine, and α-nitro-β-naphthol from β-naphthylamine. In attempting to prepare p-bromphenol from p-brom-aniline nitrate, through the intervention of the diazo-reaction, Olivieri (*Gazzetta*, 1884, *14*, 459) employed nitrous anhydride from As_2O_3 and HNO_3 and succeeded in getting nitro-brom-phenol which result he attributed to the use of HNO_3 of too high specific gravity and to the production of NO_2 therefrom.

Attempts have been made in this paper to bring about nitration and diazotisation in one operation by means of nitrous gases produced by the action of concentrated nitric acid on arsenious oxide. A number of amino-compounds have been tried and a good yield of nitro-phenolic compounds in a fair state of purity has been obtained in several cases. This method appears to be quite suitable for the preparation of some of these nitro-compounds in the laboratory.

Thus from aniline 2:5-dinitro-phenol, from p-nitr-aniline 2:4-dinitro-phenol, from p-chloro-aniline 2:3-dinitro-4-chloro-phenol, from p-brom-aniline 4-brom-3-nitro-phenol, from s-tribrom-aniline s-tribrom-dinitro-phenol, from o-toluidine 4-nitro-o-cresol, from 5-brom-o-toluidine 5-brom-3-nitro-o-cresol, from p-toluidine 2:6-dinitro-cresol, from m-xylidine 6-nitro-m-xylenol, from o-anisidine p-nitro-phenol-o-methyl ether, from benzidine a mono-nitro-phenolic compound, from o-amido-salicylic acid nitro-proto-catechuic acid, from o-amido-benzoic acid 3-nitro-salicylic acid, from m-amido-benzoic acid 5-nitro-3-hydroxybenzoic acid, from α-naphthyl-amine 2-nitro-α-naphthol, from β-naphthylamine 1-nitro-β-naphthol have been obtained, whilst o-nitraniline pro-duces no definite product and m-nitraniline gives yellow shining plates, the nature of which is not yet determined.

EXPERIMENTAL.

The usual procedure in carrying out these experiments has been to dissolve the hydrochloride of the base in water or the base itself in hydrochloric acid solution, or if it is not very soluble, to keep it in suspension, cool the solution or suspended mass in a freezing mixture below 0° and then pass nitrous gases for about half an hour (or less, if gases are no more absorbed), allow the reacting substances to stand for some time, in some cases overnight, and then heat on a water-bath for half an hour, allow them to cool, remove the crystals separated, recrystallise them from rectified spirit and identify them by determination of melting point and the percentage of nitrogen.

Starting material. (2g. was taken in each case.)	*Product.*
Aniline hydrochloride	Dinitro-phenol (1·5 g.).
o-Nitraniline dissolved in hydrochloric acid.	No definite product.
m-Nitraniline dissolved in hydrochloric acid.	Yellow shining plates, extremely explosive.
p-Nitraniline dissolved in hydrochloric acid.'	Dinitro-phenol (1·5 g.).
p-Chloraniline dissolved in hydrochloric acid.	2:3-Dinitro-4-chlorophenol (1·5 g.).
p-Bromaniline dissolved in hydrochloric acid.	4-Brom-2-nitrophenol, yellow plates, m. p. 89° (0·4 g).
s-Tribrom-aniline.	s-Tribrom-dinitrophenol, yellow plates, m. p. 195° (0·4 g.).
o-Toluidine hydrochloride.	4-nitro-o-cresol (2·1 g.).
5-Brom-o-toluidine dissolved in hydrochloric acid.	3-Brom-3-nitro-o-cresol (>5 g.)
p-Toluidine hydrochloride.	2:6-Dinitro-p-cresol (1·3 g.).
m-Xylidine in hydrochloric acid solution.	6-Nitro-m-xylenol (1·8 g.).

Starting material.	*Product.*
(2g. was taken in each case.)	
o-Anisidine in hydrochloric acid solution.	A small quantity of p-nitro-phenol-o-methyl ether, brownish black plates, m. p. 58°.
Benzidine hydrochloride.	A mono-nitro-derivative, m. p. 104° (1·9 g.).
o-Amido-salicylic acid in hydrochloric acid solution.	Nitro-protocatechuic acid, decomposing above 200° (1·2 g.).
o-Amido-benzoic acid in hydrochloric acid solution.	3-Nitro-salicylic acid (1·8 g.).
m-Amido-benzoic acid in hydrochloric acid solution.	5-Nitro-3-hydroxy-benzoic acid, pale yellow needles, m. p. 166° (1·2 g.).
a-Naphthylamine in hydrochloric acid solution.	2-Nitro-a-napthol, deep reddish-brown crystals, m. p. 125-127° (1·9 g.).
β-Naphthylamine in hydrochloric acid solution.	1-Nitro-β-naphthol, thin red crystals, m. p. 104° (1·9 g).

In the case of aniline hydrochloride, the reaction is vigorous and the solution is coloured deep green, changing to deep red on standing. Shining yellow plate-like crystals (m. p. 104°) are obtained from rectified spirit (Found: N=15·65. $C_6H_3(NO_2)_2OH$ requires N=15·25 per cent.).

From m-nitraniline yellow shining thin plates of extremely explosive nature are obtained. This product is not yet identified.

With p-chloraniline, brownish yellow crust is formed, the solution turning deep yellow at the same time. On crystallisation long yellow needles, m. p. 70-71°, are obtained. (Found: N=12·99; Cl=16·29. $C_6H_2(OH)(NO)_2Cl$ requires N=12·81; Cl=16·05 per cent.).

With o-toluidine, the alcoholic solution is scratched with a glass rod before fine reddish-brown needles, m. p. 81-82°, are obtained. (Found: $N = 9.30$. $C_6H_3(CH_3)(OH)NO_2$ requires $N = 9.17$ per cent.).

From p-toluidine greenish-yellow plate-like crystals, m. p. 80-81°, are obtained. (Found: $N = 14.10$. $C_6H_3(CH_3)(OH)(NO_2)_2$ requires $N = 14.15$ per cent.).

With m-xylidine, the reaction is feeble and the solid product separates on keeping in a vacuum desiccator. Brown hygroscopic plates, m. p. 92°, are obtained.

With α- and β-naphthylamines, the reacting mixtures should not be heated on water-bath above 50°, else charring takes place. In both cases good yield (about 80 per cent. of the theory) of the nitro-derivatives is obtained.

Nitration. Part III. Nitration of Naphthalene.

BY

PHULDEO SAHAY VARMA AND C. KUSHIRAMA MENON.

a-Nitro-naphthalene is a compound of great commercial importance as it is required in quantity for the preparation of a-naphthylamine and of a-naphthylamine sulphonic acids. Attempts have been made to study the methods of the preparation and see if the existing method of manufacture can be improved. The manufacture of this compound is described by Witt (*Chem. Ind.* 1887, *10*, 25) : a mixture of nitric and sulphuric acid is employed as a nitrating agent, the temperature being kept at 45—50° until towards the end when it is raised to 60°. The whole process is completed in one day. The yield is said to be about 95 per cent. of the theory. Triller (D. R. P. 100417) obtained a-nitro-naphthalene by passing an electric current through a mixture of one part of naphthalene and 50 parts of nitric acid (*d* 1·25) at 80°. Amongst other methods for the preparation of a-nitro-naphthalane, one by the action of NO_2 on naphthalene (Lecds, *J. Amer. Chem. Soc.*, 1880, *2*, 283) may be mentioned.

The part played by sulphuric acid in nitrating mixtures has not yet been satisfactorily explained. "It is generally understood that the advantage of the addition of sulphuric acid is to absorb the water formed during nitration and thus to keep the nitric acid from being too dilute. The stronger the acid and the higher the temperature, the larger the amount of nitro-groups introduced".

(Sudborough: Bernsthen, "Organic Chemistry.") If this is true, there is no reason why mechanical absorbents of water should not equally serve the purpose, but so far as the nitration of benzene is concerned this is not the case, as in experiments that have been carried out in this laboratory in which the place of sulphuric acid has been taken by plaster of Paris and such other substances, no improvement in the nitration of benzene has been observed. But so far as the nitration of naphthalene is concerned the case has been found to be different. In this case plaster of Paris and quick-lime have been found equally effective in removing the water formed during the reaction and in giving as good a yield of nitro-naphthalene as that obtained in presence of sulphuric acid.

In addition, a number of other agents, some of them never tried before on naphthalene, have been tried with a view to ascertain their utility in nitration. The various nitrating agents used in the experiments described in this paper are given below with the yield of α-nitro-naphthalene obtained therefrom. Five g. of naphthalene were treated in each case.

Expt.	Nitrating Agent.	Yield of α-nitronaph.	
		In grams.	In per cent.
1	Conc. HNO$_3$ alone	4·7	70
2	Conc. HNO$_3$ + Conc. H$_2$SO$_5$ (5 c.c.) ...	5·8	86
3	Conc. HNO$_3$ + acetic anhydride (0·5g) ...	5·2	77
4	Conc. HNO$_3$ + quicklime (0·5g) ...	5·8	86
5	Conc. HNO$_3$ + plaster of Paris (0·5g) ...	5·6	86
6	Conc. HNO$_3$ + P$_2$O$_5$ (0·5g) ...	5·8	86
7	Fuming HNO$_3$ + Nitro-sulphonic acid ...	5·4	80
8	NaNO$_3$ + Conc. H$_2$SO$_4$ ...	5·5	81
9	NaNO$_2$ + dilute H$_2$SO$_4$	2·0	43
10	NO$_2$	0·5	7
11	NO	0·2	3
12	N$_2$O$_3$	4·2	73

It is obvious from the data given above that the same yield of a-nitro-naphthalene is obtained by using nitric acid either in presence of conc. sulphuric acid or of phosphorous pentoxide or of quick-lime or of plaster of Paris. Sodium nitrate and conc. sulphuric acid and a mixture of fuming nitric and nitro-sulphonic acids also produce good yields. It is interesting to note that neither NO nor NO_2 gives appreciable yields of nitro-naphthalene whilst N_2O_3 produces a good yield.

In certain cases a mixture of a-nitro-naphthalene and naphthalene was obtained as the final product. Here difficulty was experienced in ascertaining the proportion of the two constituents in the mixture without involving considerable loss in separation and purification. This difficulty was got over by finding out the boiling points of a mixture of a-nitro-naphthalene and naphthalene and drawing a curve therefrom. With the help of this curve it is possible to have a rough idea of the amount of the two constituents in the mixture.

EXPERIMENTAL.

Variation in the Boiling point of a Mixture of Naphthalene and a-Nitro-naphthalene :—five g. of naphthalene were placed in a dry test tube the mouth of which was closed by a loose plug of cotton wool through which passed a thermometer. The test tube was put inside an iron chimney so that the bottom was just above the surface of the wire-gauze placed at the bottom of chimney. The gauze was then heated with a steady flame and the boiling point of the substance in the test-tube was quickly and carefully noted so as to avoid loss of material by evaporation. The cotton was removed, different quantities of a-nitro-naphthalene introduced, the mouth of the test-tube quickly closed and the boiling point noted.
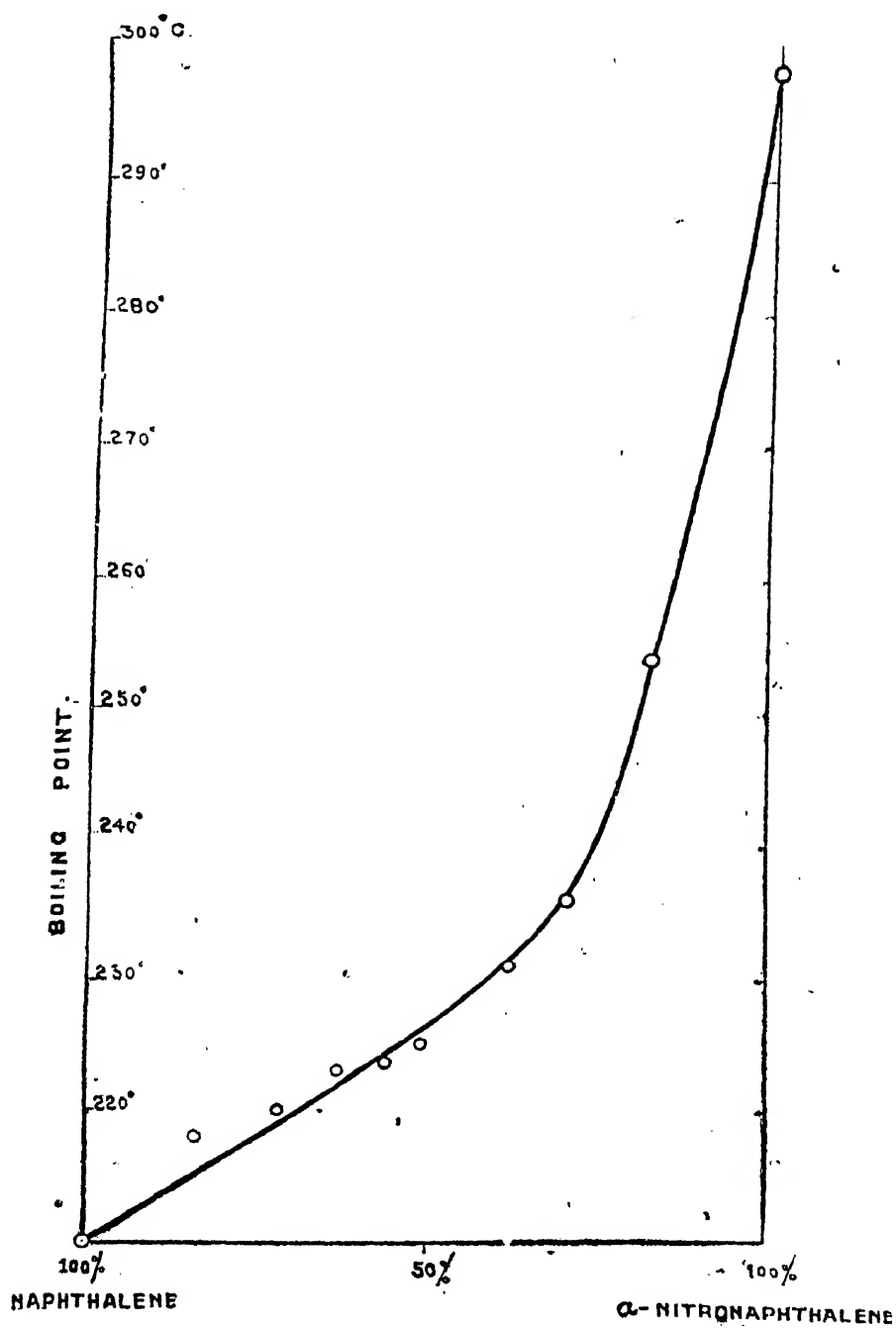
The experiments were repeated with 5 g. of pure α-nitro-naphthalene at the outset and determination of the points made successively when no naphthalene was present and when 1, 2, 3, 4 and 5 g. of naphthalene were successively added. The results obtained are recorded below :—

Naphthalene. (in gms.)	α-Nitro-n aphthalene.	Boiling point.	Percentage of α-nitro- naphthalene.
0	5	298°	100
1	,,	254°	83·3
2	,,	236°	71·4
3	,,	231°	62·5
4	,,	227°	55·5
5	,,	225°	50
5	,,	225°	50
,,	4	223·5°	44·5
,,	3	223°	37·5
,,	2	220°	28·5
,,	1	218°	16·7
,,	0	210°	0

The accompanying curve is drawn with the boiling points along the Y-axis and the percentage of the constituents along the X-axis.

A Mixture of Concentrated Sulphuric and Nitric Acids.—Concentrated nitric acid (*d.* 1·42; 5 c.c.) was mixed with concentrated sulphuric acid (5 c.c.) in a flask of 100 c.c. capacity. The flask was placed on a water-bath and powdered naphthalene (5 g.) was added gradually during the course of ten minutes. The mixture was well-stirred after each addition, the temperature being maintained at 40-50°. After every addition of naphthalene there was an evolution of brown fumes of nitrous gases. When the whole of the naphthalene had been added the temperature was gradually raised to 60° and maintained for half an hour. The contents were then allowed

to cool. The reddish-yellow cake was freed from the adhering liquids and crystallised from rectified spirit, m. p. 58-5°. Yield 5·8 g. of α-nitronaphthaleme.

Concentrated Nitric Acid :—Naphthalene (5 g.) was added gradually to concentrated nitric acid (d 1·42; 5 c.c.). The subsequent operations were the same as in the preceding case. Yield of α-nitro-naphthalene was 4·7 g.

Nitric Acid in Presence of Acetic Anhydride :— Naphthalene (5 g.) was mixed thoroughly with acetic anhydride (0·5 g.) and concentrated nitric acid (5 c.c.) was added drop by drop with continuous stirring in about five minutes, the vessel being cooled from time to time to prevent rise of temperature above 50°. When the whole of the acid has been added, the mixture was warmed to 60° for half an hour, cooled, freed from the adhering acid and crystallised. Yield 5·2 g. By using 1 g. instead of 0·5 g. acetic anhydride the yield was 5·6 g.

Nitric Acid in presence of Quick-lime, of Plaster of Paris and of Phosphorus Pentoxide:—Similar experiments using (a) 1·0 and 0·5 g. of quick-lime, (b) 1·0 and 0·5 g. of plaster of Paris and (c) 1·0 and 0·5 g. of phosphorus pentoxide gave in each case 5·8 g. of α-nitro-naphthalene from 5 g. of naphthalene.

A Mixture of Fuming Nitric and Nitro-Sulphonic Acid:—This mixture contained about 50 per cent. of nitro-sulphonic acid. This mixture (5 c.c.) was taken in a flask and naphthalene (5 g.) was added at intervals in five minutes. The evolution of brown fumes was very copious. The subsequent procedure was the same as in the preceding cases. α-Nitro-naphthalene (5·4 g.) and 1 : 5-dinitro-naphthalene (0·2 g.) were obtained.

Sodium Nitrate and Concentrated Sulphuric Acid :— Naphthalene (5 g.) and sodium nitrate (5 g.) were placed in a round-bottomed flask and concentrated sulphuric

acid (2 c.c.) added. The flask was immersed in an oil-bath and heated gradually in an hour to 100°, adding in the mean time 3 c.c. more of sulphuric acid. The contents were thoroughly stirred. Naphthalene melted and gradually turned deep red. After being heated for 10 minutes more, the flask was allowed to cool and the solid cake washed several times with water and crystallised. Yield of α-nitro-naphthalene, 5·5 g.

Sodium Nitrite and Dilute Suphuric Acid :—Powdered naphthalene (5 g.) was suspended in dilute sulphuric acid (50 c.c.) in a round-bottomed flask on oil-bath. Finely-powdered sodium nitrite (5 g.) was added at intervals with stirring. Brown fumes were evolved and on raising the temperature, molten naphthalene changed to a yellowish and then to a brownish colour. The reaction was more vigorous at 109-110°. When the whole of sodium nitrite was added the flask was heated for half an hour more and allowed to cool. The solid product crystallised from rectified spirit. Yield 2·9 g.

Nitrogen Peroxide :—This peroxide was led into the flask containing naphthalene (5 g.). The gas was passed for about 45 minutes. No action took place in the cold but when the naphthalene melted, some action took place. The flask was cooled and the product crystallised. The boiling point of the product was found to be 230°. Therefore only 0·5 g. of α-nitro-naphthalene is present.

Nitric Oxide :—This oxide was led into molten naphthalene (5 g.). Only 0·2 g. of α-nitro-naphthalene was found in the product.

Nitrous Gases :—Nitrous gases, prepared by the action of nitric acid on arsenious oxide, were led into naphthalene (5.g.) which was attacked slowly at the outset but vigorously later on when naphthalene melted by the heat evolved in the reaction. The flask was cooled to prevent too much heating. The gases were

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passed for half an hour and the contents of the flask heated for another half an hour at 60° and allowed to cool. The crystalline product (4·9 g.) was found to be α-nitro-naphthalene.

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      BENARES

Adsorption by Polar Precipitate. Part III. Electro-osmotic Experiments with Silver Iodide.

By

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In a recent paper on the adsorption of ions by freshly prepared lead chromate, it has been pointed out (Mukherjee and Roy, *J. Indian Chem. Soc.*, 1924, *1*, 173) that electro-osmotic experiments give us a better idea of the adsorption of ions than analytical methods. They point out that the latter do not give any indication as to whether the adsorbed ions replace those of the same sign in the crystal lattice thus leaving the crystal and its surface electrically neutral, or are adsorbed on the surface (without exchange of ions) which consequently becomes electrically charged through an excess of the adsorption of ions of one sign. Electro-osmotic measurements enable us to follow the relative adsorption of ions of both sign. It has also been pointed out that analytical methods give an idea of the net exchange of ions between the double layer and the solution, but our observations on the variation of the charge on the surface give us an idea of the adsorption of ions of both sign in the fixed layer of ions on the surface (Mukherjee and Ghosh, *J. Indian Chem. Soc.*, 1921, *1*, 213). Taylor and Beekley (*J. Phys. Chem.*, 1925, *22*, 912) have recently measured by analytical methods the adsorption of ions by precipitated silver iodide. They point out the desirability of studying the adsorption of substances by chemically pure subtances

and they worked with silver iodide as it can be prepared in a very pure condition.

In the present paper the results of experiments with silver iodide similar to those already carried out with lead chromate are recorded.

EXPERIMENTAL.

The arrangement we used for electro-osmotic measurements is a modified form of that used by Briggs (Mukherjee and Roy, *J. Indian. Chem. Soc.*, 1924, *I*, 173).; The results are reproducible within ± 7 per cent. The precipitate was shaken with water or electrolyte in a stopper Jena glass bottle, kept for 24 hours and then poured in the U-tube. The precipitate being heavy settled within an hour.

The preparation and purification of the precipitate require great care and in this matter, the procedure described by Taylor and Beekley (*loc. cit.*) has been scrupulously followed. The silver iodide thus obtained was found to be free from adsorbed and occluded salts, and to be quite insensitive to light as stated by the above authors.

The results are given in Tables I and II. The figures give the movement of the bubble in cm. per minute. The sign indicates the sign of the charge carried by the particles. The concentrations are given in gram equivalents per litre. At concentrations higher than those in the table, the results become unreliable on account of electrolysis.

TABLE I.[1]

Electrolytic concentration.	AgNO₃	KCl	K₂SO₄	KBr	KI
0	−6·6	−6·6	−6·6	−6·6	−6·6
·0001	+·7·3	−11·4	...		
·0002	+8·1	−12·9	−15·3		−12·5
·0004	+10·5	−15·3	...		−12·7
·001	12·5	−6·7	−18·2	−21·7	−15·0
·002	electrolysis	−18·2	−19·4	−20·8 (?)	electrolysis
·004	...	−20·2	−18·7	−23·0	

TABLE II.

Electrolytic concentration.	KI	KNO₃	Ba(NO₃)₂	Ca(NO₃)₂	Al(NO₃)₃
0	−3·9	−3·9	−3·9	−3·9	−3·9
·0002	−9·9	−13·1	−6·2		
·001	−13·8	−16·8	−8·5	−8·7	−4·5
·002		−18·4	−9·8	−9·9	−4·5
·004		−19·1	−9·6	−10·0	−3·5

DISCUSSION.

A. Change in Contact with Water.

We find that, similar to what has been observed in the case of lead chromate, purified silver iodide is negatively charged in contact with water. In view of the case taken to prepare the substance free from

[1] A different sample of silver iodide was used in this experiment.

electrolytes and the fact that silver nitrate was present in excess at the time of precipitation, one may assume that the negative charge is not due to an adsorption of an excess of iodine ions by the surface. If this be true, then the initial negative charge may be ascribed to either of two sources :

(1) A preferential adsorption of hydroxyl ions from water, or (2) what appears more probable on theoretical grounds, silver ions are perhaps held less strongly on the surface than iodine ions. It is possible to imagine that some of the silver ions on the surface, in virtue of their thermal energy, loosen themselves from the lattice and form the mobile sheet of the double layer.

From the point of view of the latter alternative all that we need assume is that at any instant under consideration a number of silver ions remain near the surface in a mobile state and take part in the conduction of electricity when a potential gradient acts along the surface. The assumption that the iodine ion is more intensely held in the lattice than the silver ion is in keeping with the well-known fact than the transference of electricity in solid silver iodide and many other salts takes place mainly through the positive ion. However we shall see presently that iodine ions are apparently less strongly adsorbed than silver ions and that further work is necessary before we can be sure as to the validity of this explanation.

B. Adsorption of Constituent Ions.

Unlike the case of lead chromate we find that, of the constituent ions though silver ions are adsorbed much more strongly than the other cations we have used, iodine ions are adsorbed less strongly than most of the other univalent anions. The intensity of adsorption of silver

ions is apparent from the fact that at a concentration of 0.001 normal, the rate of electro-osmotic flow has changed from 6·6 to 12·5, whereas at the same concentration, the adsorption of iodine ions has increased the rate of flow from 6·6 to 15·0. The weakness of the adsorption of iodine ions is unexpected and difficult to account. Even assuming that the initial negative charge is to be ascribed to the excess of iodine ions on the surface over silver ions, the magnitude of the change in the positive charge points to a stronger adsorption of silver ions. Further the nitrate ion is more strongly adsorbed than other anions and taking this into consideration, we find that adsorption of silver ions is greater than that indicated by the rate of electro-osmotic flow. It is also not possible to refer the weak effect of iodine ions to strong adsorption of potassium ions, as it is well known that alkali metal ions are not primarily adsorbed (*cf.* Mukherjee and Ray, *J. Chem. Soc.*, 1924, *125*, 476) while the electro-osmotic data point to weak adsorption of iodine ions, we are prevented from drawing a definite conclusion, as we have also observed that in the presence of potassium iodide the precipitate breaks up into smaller particles. Until the increased frictional resistance that is to be expected from a diminution in the size of the particles has been taken into account, the question must be left open.[1]

C.   Adsorption of other Ions.

As usual we notice the valency effects of cations on the negatively charged surface. So far as we could observe visually we found that the other electolytes do

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[1] Hitherto, all methods which have been used for measuring the rate of electro-osmotic flow overlook this source of error. An apparatus, obviating this and other sources of error in the measurements, has been devised in this laboratory but it has not yet reached a convenient form.

not produce a change in the size of the particles of the precipitate. Comparing the different potassium salts other than the iodide we observe that bromide increases the negative charge to the greatest extent.

Taking into account the differences in the negative charge of the two samples of silver iodide it appears that the nitrate ion is more adsorbed than the chloride ion. Considering also that the adsorption of a sulphate ion means an increase of two units of negative charge, the adsorption of sulphate ion is weakest of the anions we have used. The order of adsorption of anions therefore appears to be bromide > nitrate > chloride > sulphate. Excepting the nitrate, the order is the same as that of increasing solubility. As with lead chromate we notice that the nitrate is more adsorbable and that the solubility of the nitrate gives us no idea as to the adsorbability of the nitrate ion. We observe that, barring the iodide, these results are very similar to what has been observed with lead chromate. The solubility of the corresponding salt appears to be one of the factors determining the intensity of adsorption, though it is evident that other factors have also to be considered. Lastly we would point out that electro-osmotic experiments give us an idea of the relative adsorption of the cation and anion on the surface, whereas analytical measurements of adsorption give us an idea of the adsorption as a whole in the double layer.

Summary and Conclusion.

(a) Purified silver iodide carries a negative charge in contact with water.

(b) Of the cations—silver, potassium, calcium, barium, aluminium—silver reverses the charge on the surface and imparts a strong positive charge to it and the order of adsorption is Ag > Al > Ba ; Ca > K.

(c) As opposed to the well known strong adsorption of constituent ions we have observed that the iodine ion is very weakly adsorbed by silver iodide. This is surprising in view of the observations of Lottermoser and of Fajans and Beekerath (*Z. Physikal Chem.*, 1921, *97*, 478) that constituent ions are strongly adsorbed by insoluble silver salts. It has been pointed out, however, that diminution of the size of the particles takes place when the precipitate is in contact with potassium iodide and, the increased frictional resistance may explain our observation.

(d) Of the other anions the order of adsorption appears to be $Br' > NO_3' > Cl'\ SO_4''$.

(e) Attention has been drawn to the necessity of simultaneous measurement of frictional resistance of the diaphragm in electro-osmotic experiments—a source of error not taken into consideration in the methods of measurement which are in use.

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Halogenation, Part II.   Direct Iodination in Presence of Sodium Nitrite and Fuming Sulphuric Acid.

BY

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In a previous communication Varma and Kulkarni, (this *Journal* page 291) it has been shown that iodine can be introduced directly into the benzene nucleus by means of a mixture of fuming nitric and nitro-sulphonic acids and that the presence of a small quantity of glacial acetic acid in addition, increases the yield of the iodo-derivatives to a considerable extent. This investigation has been continued further and it has been found possible to introduce iodine directly into the benzene nucleus in presence of sodium nitrite and fuming sulphuric acid.   Ordinary concentrated sulphuric acid may be used instead of the fuming acid, but the yield is smaller.   In this case also glacial acetic acid (2 c.c.) increases the yield of the iodo-compound.   Experiments have been made in order to find the proportions that produce the maximum yield of iodo-benzene and the proportions given in Expt. 5 have been found to give the maximum yield.   It is possible to get 11.5 g. of iodo-benzene from 10 g. of benzene which comes to about 70 per cent. of the theory.   Some benzene remains unacted upon.   Any attempt to convert this remaining benzene into iodo-benzene, by heating for a longer period or by changing the proportions of the reacting materials, results in the formation of poly-iodo-derivatives.   The yield of

iodo-benzene obtained by this method is better than that obtained by the methods of Datta and Chatterjee (*J. Amer. Chem. Soc.*, 1917, 39, 43) and of Varma and Kulkarni (*loc cit*). Moreover, the time taken for the operation is short, the whole can be finished in an hour and a half. Toluene and xylene have also been similarly treated and iodo-toluens and iodo-xylenes been obtained.

EXPERIMENTAL.

In the experiments tabulated below, a mixture of sodium nitrite, iodine, the hydro carbon and if necessary, glacial acetic acid is put into a round-bottomed flask, connected with a reflux condenser and heated on the water-bath. Sulphuric acid is then dropped in small quantities at a time. At the end of a specified period, the product is washed first with water then with very dilute sodium hydroxide solution and finally with distilled water. The product is then dehydrated by fused calcium chloride and distilled.

Instead of fuming sulphuric acid, a mixture of concentrated and fuming sulphuric acid has been used to find if the yield can be improved but without success (*Vide* Expts. 1 and 14). It is interesting to note that the increase of fuming sulphuric acid beyond a certain limit, keeping the quantities of other ingrediants the same, does not increase but decreases the yield of the iodo-compounds. (*Vide* Expt. 10).

The fuming sulphuric acid contained 10 per cent. sulphur trioxide.

Serial No. of Expt.	Benzene in c.c.	Iodine in grams.	Sodium nitrite in grams.	Fuming H₂SO₄ in c.c.	Conc. H₂SO₄ in c.c.	Acetic acid in c.c.	Time allowed for reaction in hours.	Yield of iodo-benzene in grams.	Unchanged hydrocarbon in c.c.	Solid residue in grams.
1	15	12	15	10	10	...	2·5	6·0	7	1
2	15	12	15	20	...	2	3·0	4·5	5	3
3	15	12	...	20	...	2	3·0	0	12	...
4	15	10	15	20	...	2	1·25	10·5	4·8	0·3
5	15	10	15	20	...	2	1·5	11·5	3·7	1·2
6	15	10	15	...	20	...	1·5	8·8	5	...
7	15	10	15	20	...	2	1·5	7·0	6	...
8	10	10	15	20	...	2	1·5	7·4	1·3	3·0
9	15	10	15	15	...	...	1·5	8·7	3	...
	Toluene							Iodo-toluene		
10	15	10	15	15	...	2	1·0	14	2·8	...
11	15	10	15	20	...	2	1·0	10	3·4	...
	m-Xylene							Iodo-xylenes		
12	15	10	15	20	...	2	0·8	10·3	2·5	...
13	15	10	15	...	20	2	0·8	7·5	9·0	...
14	15	10	15	10	10	2	0·8	8·7	5·0	...

On the Constitution of Arsenious Sulphide Sol in·Presence or Absence of Arsenious Acid.

BY

· SURODH GOBINDA CHAUDHURY

AND

· PRIYANATH KUNDU.

In a recent paper (*J. Indian Chem. Soc.*, 1925, 2, ·301) Mukherjee and Chaudhury have shown that, in the presence of acids, variations in the migration velocity of the colloidal particles of arsenious sulphide prepared under different conditions are different. Freundlich and Nathansohn (*Koll. Zeit.*, 1921, 28, 258) have suggested that the free hydrogen sulphide present in ·arsenious sulphide sols is photochemically oxidised to sulphur dioxide which again reacts with hydrogen sulphide to form pentathionic acid and sulphur. The sulphur adsorbs polythionate ions and thus passes into the colloidal sulphur. Murphy and Mathews (*J. Amer. Chem. Soc.*, 1923; 45, 16) mention that the assumption of the presence of polythionic acids is necessary to ·explain the increase in the · conductivity of the sols on exposure to light. Bhatnagar ,and Lakshan Rao have also shown ·in an interesting study (*Kol.-Zeit.*, 1923, 33, 164) that the transformation of the colour of orange sols of· arsenious sulphide into yellow is ·due to the oxidation of the particles. Accordingly it seemed desirable to investigate the constitution of different samples of arsenious sulphide sols, *as prepared and used in this laboratory.*

Experimental.

Arsenious sulphide sols were prepared, under two conditions:

(1) Equal volumes of a solution of arsenious acid prepared by diluting a saturated solution with equal volume of conductivity water, and of a saturated solution of hydrogen sulphide in conductivity water, were mixed quickly and thoroughly shaken (Sol A). That the sol A contains free arsenious acid was shown by passing hydrogen sulphide into the liquid filtered from arsenious sulphide sol after precipitation by an electrolyte.

(2) Equal volumes of a solution of arsenious acid obtained by diluting a saturated solution with equal volume of conductivity water, and of a saturated solution of hydrogen sulphide in conductivity, water were mixed quickly and thoroughly shaken. Hydrogen sulphide was then passed into the mixture till no free arsenious acid could be detected in the filtrate after precipitation by an electrolyte. Pure hydrogen was then bubbled through the colloidal solution till there was no free hydrogen sulphide (Sol B).

Portions of these sols were taken for determination of arsenic and sulphur. Twenty-five c.c. of the sol were dissolved in excess of liq. ammonia fort, oxidised by hydrogen peroxide, evaporated to dryness in a water-bath and dissolved in water. The solution containing arsenate and sulphate was filtered from impurities present in the ammonia. The precipitate was washed carefully and the wash-liquor was added to the previous filtrate. Arsenic was then estimated as magnesium pyroarsenate, and sulphur as barium sulphate. The arsenic present as sulphide in a colloidal state in sol A was found from the difference in the total arsenic and that present in the filtrate after precipitation with an electrolyte. The

arsenic not present in the colloidal state was estimated as above in same volume of the sol after removing the colloid by coagulating it.   Results are given below :

In column II are given the number of gram atoms of arsenic present as colloidal sulphide in 25 c.c. sol.   In column III are given the number of gram atoms of sulphur which have combined with the number of atoms of arsenic given in column II to form the sulphide.   The ratio between them is given in column IV.

	II	III	IV.
Sol. A.	0·0007975	0·001163	1 : 1·46
Sol. B.	0·001213	0·002416	1 : 2

Discussion.

The constitution of sol A, where arsenious acid was in excess, corresponds to orpiment, arsenic trisulphide. The constitution of sol B, where arsenious acid as well as hydrogen sulphide was absent, corresponds either to As_2S_3, As_2S_5 or to As_2S_3, H_2S. The latter formula As_2S_3, H_2S is the more probable one because very little or none of the pentasulphide is formed in the absence of any acid. Bhatnagar and Lakshan Rao (*loc. cit.*) have analysed the coagulum of arsenious sulphide sols prepared in a manner similar to sol B but in the dark and have found it to be of the composition As_2S_2, xH^2S.

They have also suggested that arsenious trisulphide found on exposure to light in the coagulum is formed by the oxidation of As_2S_2, H_2S as represented below :

$$As_2S_2 x H_2S + xO = As_2S_3 + xH_2O + (x-1) S_4$$
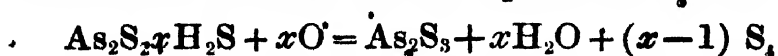
The possibility of such a reaction in the present case seems to be remote. Our results show that in diffused light As_2S_3, H_2S is formed when prepared in presence of excess of hydrogen sulphide. This substance gives out

free hydrogen sulphide, and the oxidation referred to by previous authors is of the hydrogen sulphide thus generated. The ratio of arsenic to sulphur in the sols has been determined twice with identical results.

The composition As_2S^3, H_2S corresponds to a definite acid, meta-thioarsenious acid. Our results suggest that colloidal particles of arsenious sulphide when prepared in the presence of excess of hydrogen sulphide have the composition As_2S_3, H_2S whereas, when arsenious oxide is in excess, the simple trisulphide is formed.

Our thanks are due to Prof. J. N. Mukherjee, D.Sc., for his interest in this work.

The Influence of the Dielectric Constant of the Medium on the Rate of Coagulation of Arsenious Sulphide Sol by Electrolytes.

BY

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AND

Sachindranath Mukherjee.

It is well known that colloids are sensitised by non-electrolytes of low dielectric constant. The present position has been summed up by Freundlich ("Kapillar-chemie," 1922, 2nd Edition, pp. 636-639, also 358-359). Weiser in a recent paper (*J. Phys. Chem.*, 1924, *28*, 1253) points out that along with the effect of the dielectric constant the possibility that the non-electrolyte influences the coagulation by interfering with the adsorption of the active ions has to be taken into consideration. It would appear from the following quotation that Weiser got his clue from Freundlich :

"Hiermit ist die Mannigfaltigkeit des Einflusses der Nichtelelektrolyte nicht erschöpft. Noch ehe die eben erörterte Sensibilisierung bekannt war, hatten Kruyt und van Duin auf eine eigentümliche Veränderung der Ko. W. beim As_2S_3-Sol durch kapillaraktive Stoffe, wie Amylalkohol, Phenol u. a., hingewiesen. Sie beobachteten bei der Flockung durch einund dreiwertige Kationen eine Ernierdrigung des Ko. W., also eine Sensibilisierung; bei zwei-und vierwertigen dagegen eine Erhöhung des Ko. W., also eine Beeinträchtigung der Flockung. Dies Verhalten lässt sich zurzeit schwer erklären. Es ist allerdingsdurchaus möglich, da die Flockung durch

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Nichtelektrolyte beeinträchtigt wird: Sie können ja durch ihre Adsorption die Adsorption des aktiven Ions herabsetzen, weil sie es von der, Grenziläche verdrängen (siehe S. 278). Es würde dann eine grössere Konzentration, also ein höherer Ko. W. nötig sein, um die Flockung einzuleiten. Wie aber Verdrängung und Sensibilisierung ineinandergreifen, dass anscheinend ein besonderer Einfluss der Wertigkeit des Kations dabei zustande kommt, ist vorläufig nicht verständlich."

Weiser has studied the precipitation by electrolytes, of negative arsenious sulphide sol, and of hydrous ferric oxide and hydrous chromic oxide sols both in presence and absence of phenol and *iso*amyl alcohol. He explains his observations by developing Freundlich's suggestions in the following manner:

"(1) The adsorption of a non-electrolyte by the particles of a sol decreases the stability of the latter in the sense that less of the precipitating ions must be adsorbed in order to decrease the charge below the critical values necessary for agglomeration and precipitation. The extent of the sensitisation depends on the concentration and adsorbability of the non-electrolyte and its dielectric constant. This effect tends to lower the precipitation value of an electrolyte. The amount of lowering is greatest for electrolytes with weakly adsorbed precipitating ions that precipitates only in relatively high concentration."

"(2) The adsorption of a non-electrolyte by particles of a sol cuts down the adsorption of the precipitating ion of the electrolyte added to produce coagulation. This effect tends to raise the precipitation value of an electrolyte."

"(3) Since the factors mentioned above have opposite effect on the precipitation value of electrolytes, it follows that depending on the conditions, the precipitation value

may be increased, decreased or may remain unchanged, in presence of a non-electrolyte."

From the above we see that the influence of the non-electrolyte is ascribed to two factors: (a) its dielectric constant and (b) its adsorption on the surface of the colloid particles. The influence of dielectric constant is explained by Freundlich (*loc. cit.*,) on the assumption that the lowering of the dielectric constant decreases *pari passu* the charge on the surface of the colloidal particle. He gives in support of this assumption some observations on ferric hydroxide sol. 'It is difficult to see how the charge can decrease with a diminution in the dielectric constant unless it is further assumed that substances of low dielectric constant have an effect on the adsorption of ions to which the origin of the charge on the surface is referred. Further both Freundlich and Weiser assume that a diminution of the charge in presence of a non-electrolyte indicates a diminution of stability on the part of the colloid. This assumption has been the basis of all theories on the coagulation of colloids by electrolytes since Hardy first pointed out the relationship between the charge and the stability. In a recent paper Mukherjee and Chaudhury (*J. Indian Chem. Soc.* 1925, *2*, 307) have measured the migration velocity of colloidal arsenious sulphide in presence of acetic, formic and oxalic acids and have found that the rate of migration does not determine the stability of the sol. Thus the sol is not coagulated by $10N$ acetic acid and it is coagulated by N hydrochloric acid; acetic acid diminishes the charge to a much greater extent at the same hydrogen ion concentration than hydrochloric acid does. They point out that a diminution in the dielectric constant brings about two effects:

(1) The electrical work, resulting from the displacement of the ions constituting the mobile sheet of the

double layer and surrounding the colloidal particles when two particles approach sufficiently near each other, will increase with a diminution of the dielectric constant. The result will be that the percentage of the total number of collisions between particles that are successful in bringing the particles so close to each other as to allow the surface forces to act and to lead to a stable aggregation will rapidly diminish. This effect will tend to stabilise the sol.

From the theory of the "electrical" adsorption (advanced by one of us) of precipitating ions it follows that the adsorbability will increase in a medium of low dielectric constant. This will sensitise the sol. The net effect will depend on the relative magnitudes of the two opposing factors.

The following experiments were undertaken with a view to investigate the subject from this point of view. Moreover it was thought desirable to compare the results obtained in presence of an electrolyte with a low dielectric constant in the light of the theories advanced to explain the mechanism of coagulation with mixtures of electrolytes.

EXPERIMENTAL.

Colloidal solutions of arsenious sulphide were prepared according to the method described in previous papers with excess of arsenious sulphide which was removed by passing a stream of hydrogen. Coagulation experiments were done by noting the time of complete disappearance of a filament of light from the time of mixing. The current consumed in illuminating the filament was kept constant (see Mukerjee and Ghosh, *J. Indian Chem. Soc.* 1924, *1*, 213). Equicoagulating concentrations of hydrochloric acid, sulphuric acid, potassium chloride, barium chloride

and aluminium chloride in presence of different amounts of methyl alcohol, ethyl alcohol, formic, acetic, propionic and oxalic acids were determined. The results are tabulated below.

TABLE I.

Arsenious Sulphide Sol—Ethyl Alcohol.

Percentage concentration of ethyl alcohol.	Electrolyte concentration in normality.					
	HCl	H$_2$SO$_4$	KCl	LiCl	BaCl$_2$	AlCl$_3$
0	0·03850	0·04985	0·05944	0·07073	0·001911	0·0002184
2·5	0·03675	0·04985	0·06064	0·07291	0·001985	0·0002146
5	0·03525	0·04985	0·06301	0·07211	0·002058	0·0002146
10	0·03400	0·04985	0·07055	0·07437	0·002278	0·0002109
15	0·03300	0·04985	0·07847	0·08021	0·002572	0·0002109
25	0·03500	0·04985	0·06618	0·08750	0·002940	0·0002033

TABLE II.

Arsenious Sulphide Sol—Methyl Alcohol.

Percentage concentration of methyl alcohol.	Electrolytic concentration in normality.					
	HCl	H$_2$SO$_4$	KCl	LiCl	BaCl$_2$	AlCl$_3$
0	0·04450	0·04927	0·06024	0·07394	0·001834	0·0001995
2·5	0·04325	0·04927	0·05909	0·07086	0·001771	0·0001957
5	0·04225	0·04927	0·05868	0·06932	0·001727	0·0001920
10	0·04050	0·04927	0·05707	0·06624	0·001624	0·0001882
15	0·03850	0·04927	0·05470	0·06316	0·001544	0·0001770
25	0·03550	0·04927	0·05070	0·06008	0·001286	0·0001581

TABLE III.

Arsenious Sulphide Sol—Acetic Acid.

Concentration of acetic acid in normality.	Electrolytic concentration in normality.					
	HCl	H$_2$SO$_4$	KCl	LiCl	BaCl$_2$	AlCl$_3$
0	0·03500	0·04900	0·05350	0·05631	0·001764	0·0002560
0·001	0·03500	0·04900	0·05200	0·055260	0·001800	0·0002446
0·01	0·03500	0·04900	0·05313	0·05313	0·001837	0·0002400
0·1	0·03500	0·04900	0·04800	0·04995	0·001874	0·0002384
2	0·035C0	0·04900	0·03800	0·04144	0·001950	0·0002334

TABLE IV.

Arsenious Sulphide Sol—Propionic Acid.

Concentration of Propionic acid in normality.	Electrolytic concentration in normality.					
	HCl	H$_2$SO$_4$	KCl	LiCl	BaCl$_2$	AlCl$_3$
0	0·0300	0·0500	0·05000	0·05631	0·001654	0·0003727
0·001	0·0300	0·0500	0·04600	0·05526	0·001654	0·0003652
0·01	0·0300	0·0500	0·04500	0·05313	0·001690	0·0003576
0·1	0·0300	0·0500	0·04125	0·04995	0·001690	0·0003352
2·0	0·0300	0·0500	0·02875	0·04144	0·001846	0·0003011

TABLE V.

Arsenious Sulphide Sol—Oxalic Acid.

Concentration of Oxalic acid in normality.	Electrolytic concentration in normality.					
	HCl	H$_2$SO$_4$	KCl	LiCl	BaCl$_2$	AlCl$_3$
0	0·03000	0·05000	0·04688	0·05630	0·001654	0·0003426
0·005	0·02850	0·04700	0·04188	0·05034	0·001690	0·0004179
0·01	0·02750	0·04550	0·03938	0·04834	0·001728	0·0004122
0·025	0·02650	0·04300	0·03688	0·04410	0·001874	0·0003915
0·05	0·02575	0·04100	0·03250	0·04037	0·001911	0·0003764

TABLE VI.

Arsenious Sulphide Sol—Formic Acid.

Concentration of formic acid in normality.	Electrolytic concentration in normality.					
	HCl	H$_2$SO$_4$	KCl	LiCl	BaCl$_2$	AlCl$_3$
0	0·03000	0·04875	0·04436	0·05237	0·001654	0·0003163
0·001	0·02975	0·04808	0·04250	0·05084	0·001654	0·0003087
0·01	0·02875	0·04725	0·04000	0·04776	0·001654	0·0002937
0·1	0·02800	0·04600	0·03625	0·04313	0·001654	0·0002636
2	0·02550	0·04250	0·02433	0·02850	0·001654	0·0002937

From the above tables we find that as a rule the coagulating concentration of aluminium chloride diminishes with increase in concentration of the added substance with the exception that in the case of oxalic acid there is at first a marked increase followed by a regular diminution. For barium chloride with one

exception (methyl alcohol) the concentration goes on increasing or remains unchanged when formic acid is the added substance. In the case of potassium and lithium chloride, for five of the added substances, the colloid appears to be sensitised excepting the case of ethyl alcohol which stabilises the colloid against coagulation by these electrolytes. It is rather peculiar that the coagulating concentration of sulphuric acid remains constant in four cases out of six. Hydrochloric acid also has a similar tendency though in a large number of cases including that of ethyl alcohol its coagulating concentration decreases.

Regarding the added substances we find that ethyl alcohol shows by far the larger number of instances of stabilisation against coagulation by electrolytes, e.g.: potassium chloride, lithium chloride, and barium chloride.

One notices from the foregoing that the behaviour of a coagulating ion cannot be predicted from its valency. The observation of Kruyt and Van Duin (*Koll. Zeit.* 1915, *17*, 123) that arsenious sulphide sols are sensitised by amyl alcohol and phenol against coagulation by uni- and tri-valent cations while, against bi- and tetra-valent cations a stabilisation is observed, cannot therefore be held to indicate a relationship between the behaviour of a cation and its valency. The observation that, with one exception, the added substance stabilises the sol against aluminium chloride is of interest in view of the fact that Weiser has disbelieved a similar observation of Kruyt and Van Duin. In the case of arsenious sulphide sol Weiser (*loc. cit.*), while explaining the difference in behaviour between potassium and barium chloride, finds it difficult to account for Kruyt and Van Duin's observation that the sol is sensitised against aluminium chloride.

Both Kruyt and Duin's and our observations prove conclusively that the simple explanation of Weiser is

insufficient. Further the conclusion that Weiser has drawn as to the displacement of adsorption of barium ion by *isoamyl* alcohol from his observation that less of barium is adsorbed when the latter is present is open to question; for, the amount of electrical charge carried by the particles determines the amount of adsorption of precipitating ions (*cf.* Mukherjee, *Faraday Society Discussion on Colloids*, Oct. 1920) and if the addition of non-electrolyte diminishes the initial charge of the colloid as has been assumed by Freundlich and by Weiser then this diminution alone may account for the small adsorption.

In this connection we would draw attention to similar observations by Mukherjee and Sen (*J. Chem. Soc.*, 1919, 115, 461) regarding the influence of hydrogen sulphide on the coagulation of arsenious sulphide sols by electrolyte (*vide* also Freundlich: "Kapillarchemie," 1922, p. 63). We are inclined to believe that in all these cases the suggestion of Ostwald and of Freundlich that the main effect of the added substance is to lower the dielectric constant of the medium remains valid. But it appears to us that no clear conception as to how the dielectric constant affects the stability of the sol exists at present. As stated in the introduction Mukherjee and Chaudhury have shown that the fundamental assumption that a diminution of charge always means a diminution in stability as measured by the coagulating concentration of the ion is wrong. A clear explanation of the results obtained by us or by Kruyt and van Duin is not possible till a comparison of electrical charges under these conditions has been carried out.

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Varying Valency of Platinum with respect to Mercaptanic Radicles.—Part IV. The Inadequacy of Werner's Theory to explain Certain Anomalous Cases.

BY

Prafulla Chandra Ráy, Bires Chandra Guha and Kshitish Chandra Bose-Ráy.

The action of chloroplatinic acid on various real and potential mercaptans and on some organic sulphides and disulphides has already been studied (*J. Chem. Soc.*, 1919, *115*, 872; *ibid*, 1922, *121*, 1283; *ibid*, 1922, *123*, 1331. Recently (*J. Indian Chem. Soc.*, 1925, *2*, 178) a series of complex bodies derived from chloroplatinic acid and ethyl sulphide under different experimental conditions have been described. The compounds may be tabulated as follows :

    (*a*) Et_2S, PtCl.

    (*b*.) $(Et_2S)_2$, $PtCl_2$—Six isomers of this composition have been isolated.

    (*c*) $2Et_2S$, $PtCl_3$.

    (*d*) $2Et_2S$, $PtEl_4$.

    (*e*) $2Et_2S$, $PtEl_5$, $2H_2O$.

Some of these compounds have already been discovered by other workers (Blomstrand, *J. pr., Chem.*, 1888, [ii], *38*, 852; Tschugaeff and Malschewsky, *Z. anorg. Chem.*, 1924, *135*, 385; Loir, *Ann. Chim. Phys.*, 1853, *39* (iii),

441 *etc.*). 'The action of organic bases on these bodies, which forms the subject of the present paper, affords some valuable evidence bearing on their constitutions. A part of the work describing the action of ammonia and pyridine on a few of these compounds has been already described (this *Journal*, 1926, *3*, 155). In most cases these reactions point unmistakably to the Werner constitution of these complex bodies. In the present paper the work has been extended and the action of primary, secondary and tertiary bases like aniline, benzylamine, ethylamine, piperidine, diethylamine, pyridine, and quinoline has been described.

Action of Bases on $PtCl_2, 2Et_2S.$

Ammonia, acting on most of the isomerides of the above formula, gives one and the same compound, namely, $PtCl_2, 4NH_3$. Similarly ethylamine acting on the isomers of m.p.'s 104° and 77° gives $PtCl_2, 4C_2H_5NH_2$, and benzylamine reacts with the varieties of m.p.'s 96°, 77° and 104° yielding the same compound, $PtCl_2, 4C_7H_7NH_2$, while quinoline acting on the isomer of m. p. 77° gives $PtCl_2, 2C_9H_7N$ and diethylamine with the compound of m. p. 108° yields $PtCl_2, Et_2S, NHEt_2$. Pyridine acts on the compound of m. p. 77° giving $PtCl_2, 2Py$ and $PtCl_2, 4Py$. All these reactions can best be represented on the Werner basis, thus :

where

$$B = NH_3, \ EtNH_2, \ C_7H_7NH_2$$

and

$$B' = C_9H_7N.$$
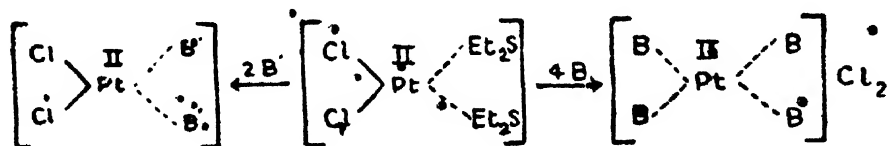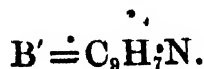
With pyridine, evidently, both the reactions take place, while with diethylamine ethyl sulphide is only partially replaced. All these compounds, however, come under the general category. The compounds with ammonia and pyridine have been already described and that with ammonia has been shown (*loc. cit.*) to have chlorine ions in aqueous solution, as expected from theory.

Action of Bases on $PtCl_3, 2Et_2S.$

This compound has been found to be split up by crystallisation from alcohol into $PtCl_4, 2Et_2S$ and $PtCl_2$ $2Et_2S$ (*J. Indian Chem. Soc.*, 1925, 2, 178) showing that $PtCl_3, 2Et_2S$ is a molecular compound of the formula $[PtCl_2, 2Et_2S], [PtCl_4, 2Et_2S]$. This is further confirmed by a study of the action of ammonia, pyridine, aniline, and benzylamine on it. Ammonia has already been shown to give $PtCl_2, 4NH_3$, which has obviously been derived from the interaction of ammonia with the first component of the molecular compound depicted above. The product of the action of ammonia on the other component has not yet been isolated. Pyridine acting on $PtCl_3, 2Et_2S$ produces $[PtCl_3, 2Py], [PtCl_2, 4Py]$ and another compound which could not be isolated in a state of perfect purity but which appears to be $PtCl_4, 2Py$. Benzylamine and aniline acting on this compound give $PtCl_2, 4C_7H_7NH_2$ and $PtCl_2, 2PhNH_2$ respectively. (The other proposed formula for this compound namely, $[Pt(Et_2S)_4]PtCl_6$ (*cf.* Tschugaeff, *Zeit. anora. Chem.* 1913, 82, 420), though it can give rise to the compound $PtCl_3$, 2Py, cannot be expected to produce compounds of the type $PtCl_2, 4Py$ and $PtCl_4, 2Py$, unless the compound first formed, namely, $[PtPy_4]PtCl_6$ is supposed to break up into

$$\left[Pt \begin{matrix} Cl_2 \\ Py_2 \end{matrix} \right] \text{ and } \left[Pt \begin{matrix} Cl_4 \\ Py_2 \end{matrix} \right].$$
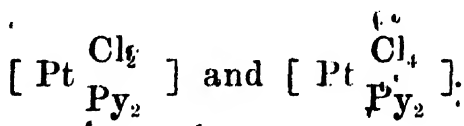
Action of Bases on $PtCl_4$, $2Et_2S$.

Ammonia and pyridine have already been shown to produce $PtCl_4$, $4NH_3$ and $PtCl_4$, $2Py$ respectively by interaction with this compound. These reactions point obviously to the Werner constitution of the body :
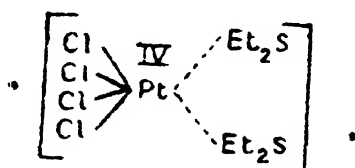
But benzylamine and aniline, as shown here, react somewhat abnormally. Benzylamine gives $PtCl_2$, $4C_7H_7NH_2$, and aniline two isomers of $PtCl_2$, $2PhNH_2$, besides aniline hydrochloride. It is quite possible that during the reaction the platinic platinum is reduced to the platinous condition as platinic chloride behaves as an oxidising agent towards organic substances, aniline hydrochloride being formed in the process.

Action of Bases on $PtCl$, Et_2S.

While Werner's theory can adequately represent the structures of the compounds ($PtCl_2$, $2Et_2S$), ($PtCl_3$, $2Et_2S$) and $PtCl_4$, $2Et_2S$, it is not possible to represent the compound $PtCl$, Et_2S as a well-defined co-ordination compound. By the action of bases like benzylamine, pyridine, peperidine and ethylamine it gives the following compounds :—($PtCl_2$, $4C_7H_7NH_2$), (Pt_2Cl, $C_7H_7NH_2$, Et_2S), ($PtCl_2$, $2C_5H_5N$), (Pt_2Cl, C_5H_5N, Et_2S), (Pt_2Cl, $2C_5H_{11}N$, $\frac{1}{2}Et_2S$), ($PtCl_2$, $4EtNH_2$) and (Pt_2Cl, $EtNH_2$, Et_2S), in all of which the type persists. The production of the above compounds shows that replacement of ethyl sulphide by the molecules of the base occurs but partially. Some intermediate compounds like these are known and have

been studied by Klason and others (*Ber.*, 1875, 28, 1496; *J. pr. Chem.*, 1903, [2] 67, 53, 39; *Ber.*, 1904, 37, 1359 etc.). $PtCl, Et_2S$ is thus simultaneously oxidized and reduced—a phenomenon which is rather extraordinary in this series of platinum compounds. As the compound is very soluble in chloroform, its molecular weight was ascertained by the ebullioscopic method and found to be 684, the theoretical value required by $2(PtCl, Et_2S)$ being 645. This formula also does not appear to admit of representation according to the co-ordination theory. It is possible, however, to represent it as follows :

$$Cl——Pt——Pt——Cl$$
$$\parallel \qquad \parallel$$
$$SEt_2 \quad SEt_2$$
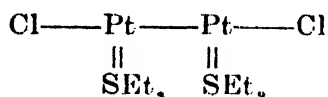
which may explain the production of the peculiar compounds (*vide supra*) with two atoms of platinum in one and the same molecule. The actual mechanism of the above reactions is still uncertain and more work must needs be done in this line before its structure can be fully elucidated.

The compound $PtCl_3, 2Et_2S, 2H_2O$, also does not apparently come under the co-ordination theory. Pyridine breaks it up and yields a compound of the formula $PtCl_4, 2C_5H_5N$. But ethylamine gives a compound, $PtCl_5, 2C_2H_5NH_2$ in which the $PtCl_5$ residue remains intact. From this meagre and apparently conflicting evidence it is not possible to assign a constitution to this peculiar compound. Further investigation regarding the action of bases on this compound is, however, in progress.

EXPERIMENTAL.

Interaction of $PtCl_2, 2Et_2S$ (m.p. 77°) *with Benzylamine.*

The compound, dissolved in a small quantity of the base, was heated on the water-bath for 15 to 30 minutes.

A strong odour of ethyl sulphide was perceptible. On cooling colourless needles separated out which were filtered and washed with a little benzylamine and then thoroughly with alcohol. The substance melts at 196°. It can be recrystallised from chloroform. (Found : Pt=28·63; Cl=10·6 ; N=8·49. $PtCl_2, 4C_7H_7NH_2$ requires Pt=28·30; Cl=10·20 : N=8·04 per cent.)

Interaction of $PtCl_2$, *2Et₂S (m.p. 96°) with Benzylamine.*

The same compound was obtained as in the previous case. The method was also the same. (Found : Pt= 28·5; Cl= 10·66 per cent.)

Reaction of $PtCl_2$, *2Et₂S (m.p. 104°) and Benzylamine.*

The same compound was obtained as above. (Found : Pt=27·5 per cent.)

Interaction of $PtCl_2$, *2Et₂S (m.p. 104°) with Ethylamine.*

The platinum compound was treated with alcoholic ethylamine, and the corked flask kept in ice-water for two hours. It was then evaporated spontaneously and the residue dissolved in warm water and concentrated in a desiccator over sulphuric acid. Colourless crystals were obtained, which were filtered and washed with a little water. The substance melts at 142°. (Found : Pt=44·1; Cl=16·5. $PtCl_2, 4EtNH_2$ requires Pt=43·9; Cl=15·8. per cent.)

Interaction of $PtCl_2$, *2Et₂S (m.p. 77°) with Ethylamine.*

The procedure was the same as above. The solution after concentration in a vacuum desiccator gave colourless crystals charring at 200°. (Found: Pt=43·7 ;. Cl= 15·86. $PtCl_2, 4EtNH_2$ requires Pt=43·9; Cl=15·8 per cent.) The mother liquor on complete evaporation left a residue which could be crystallised from a mixture of

alcohol and ether. It has not, however, been sufficiently purified for analysis.

Reaction of $PtCl_2$, $2Et_2S$ (m.p. 108°) with Diethylamine.

The mixture of the two was heated for five minutes on water-bath when the platinum compound went into solution. On filtering and allowing to stand in a desiccator, yellow crystals were deposited which had the m.p. 176°. (Found : $Pt=46\cdot6$; $Cl=17\cdot2$; $N=3\cdot55$. $PtCl_2$, Et_2S, $NHEt_2$ requires $Pt=45\cdot7$; $Cl=16\cdot5$; $N=3\cdot24$ per cent.)

Interaction of $PtCl_2$, $2Et_2S$ (m.p. 77°) with Quinoline.

A mixture of the two was heated on the water-bath for about half an hour. The platinum compound dissolved and after cooling it was precipitated with ether. The yellow substance was then re-crystallised from boiling alcohol. It melts at 165°, solidifies on cooling and with further rise in temperature it begins to redden and slightly chars just below 280°. (Found : $Pt=38\cdot3$; $Cl=12\cdot8$. $PtCl_2$, $2C_9H_7N$ requires $Pt=37\cdot5$; $Cl=13\cdot5$ per cent.)

Reaction of $PtCl_3$, $2Et_2S$ with Pyridine.

The platinum compound was heated for five hours under reflux with excess of pyridine. The deep orange colour of the substance slowly changed to pale orange. It was then filtered hot, and washed thrice with boiling pyridine. The residue was extracted thrice with boiling water and filtered, and was finally washed with alcohol and dried. It was insoluble in all solvents including chloroform and nitrobenzene. (Found : $Pt=42\cdot3$; $Cl=23\cdot29$; $N=5\cdot78$. $PtCl_3$, $2Py$ requires $Pt=42\cdot7$; $Cl=23\cdot09$; $N=6\cdot07$ per cent.) The hot pyridine extract

on standing for 24 hours spontaneously deposited a mass of colourless needles. These were washed with a little pyridine and then with anhydrous alcohol. The compound is highly soluble in water and does not melt or char up to 260°. (Found: $Pt = 32·4$; $Cl = 11·82$; $N = 10·1$. $PtCl_2, ·4Py$ requires $Pt = 33·3$; $Cl = 12·1$; $N = 9·6$ per cent.) The aqueous extract on concentration and cooling deposited a yellow compound, which is probably impure $PtCl_4, 2Py$. (Found: $Pt = 41·6$; $Cl = 27·7$. $PtCl_4, 2Py$ requires $Pt = 39·6$; $Cl = 28·7$ per cent.).

Interaction of $PtCl_3, 2Et_2S$ with Benzylamine.

$PtCl_3, 2Et_2S$ was heated with benzylamine for 1—2 hours. The solution was then treated with alcohol and filtered. The precipitate was thoroughly washed with alcohol. It was crystallised from chloroform and a mixed melting point determination with the compound obtained from $PtCl_2, 2Et_2S$ (m.p. 37°) and benzylamine (vide supra) showed no depression. (Found: $Pt = 28·23$; $N = 8·25$. $PtCl_2, 4C_7H_7NH_2$ requires $Pt = 28·3$; $N = 8·04$ per cent.)

Reaction of $PtCl_3, 2Et_2S$ with Aniline.

The compound was treated with aniline, the mixture shaken up and allowed to stand. The colour of the solution turned orange and then red. On treatment with ether a tarry precipitate came down, which, when boiled with acetone, changed to a yellow granular mass, which was filtered, washed with a little acetone and alcohol and then dried. (Found: $Pt = 43·88$; $Cl = 16·5$. $PtCl_4, 2PhNH_2$ requires $Pt = 43·3$; $Cl = 15·6$ per cent.)

Interaction of $PtCl_4, 2Et_2S$ with Benzylamine.

The compound was treated with a small quantity of benzylamine, when in a minute or two the colour of the

solution darkened with evolution of heat and the smell of ethyl sulphide was given out. It was heated for half an hour on the water-bath, when colourless crystals appeared, which were filtered and washed first with a little benzylamine and then thoroughly with alcohol. It could be recrystallised from chloroform, and it proved to be identical with $PtCl_2$, $4C_7H_7NH_2$ described above. (Found: $Pt = 27·8$; $PtCl_2$. $4C_7H_7NH_2$ requires $Pt = 28·3$ per cent.)

Interaction of $PtCl_4$, $2Et_2S$ with Aniline.

The platinum compound was treated with excess of aniline and the mixture heated for half-an-hour on the water bath, when a dark violet viscous solution was obtained. The smell of ethyl sulphide was perceptible. It was cooled and then precipitated by ether. The ethereal extract was kept for subsequent treatment. The pasty mass, thrown down, was filtered and washed repeatedly with ether and then dried and extracted with warm water. The aqueous extract on concentration in a vacuum desiccator gave a small quantity of gray crystals (m. p. 100°) which were filtered and dried (Found: $Pt = 43·4$; $Cl = 14·83$. $PtCl_2$, $2PhNH_2$ requires $Pt = 43·17$; $Cl = 15·00$ per cent.). The mother-liquor on further concentration gave a crystalline precipitate which proved to be pure aniline hydrochloride as shown by analysis and a mixed melting point determination. The residue after washing with water was found to be partially soluble in benzene and acetone, but the substance extracted by these solvents could not be purified sufficiently for analysis. The ethereal extract (vide supra) after spontaneous evaporation left a residue, which was washed with a little ether to remove the aniline. The magenta-coloured residue was washed with warm alcohol. The residue became yellow and could be

crystallised from a large volume of acetone. It melts at 190°. and changes to a brown solid, which chars above 205° (Found: Pt = 43·46; Cl = 15·63. $PtCl_2$, $2PhNH_2$ requires Pt = 43·17; Cl, 15·60 per cent.).

Action of Benzylamine on $PtCl$, Et_2S.

The platinum compound with benzylamine (in excess) was heated on water-bath for three hours. The colour of the mixture darkened. It was then filtered, and the residue washed twice with hot benzylamine, and then thoroughly with alcohol, when a crystalline white substance was left behind. This was first boiled with alcohol and filtered; the filtrate on concentration and cooling gave a nearly white crystalline compound, which, however, being very small in quantity did not admit of purification and analysis. It melts at 110°, becomes semisolid and chars above 205°. The residue after extraction with alcohol was repeatedly crystallised from chloroform in colourless needles which were found to be identical with $PtCl_2$, $4C_7H_7NH_2$ mentioned above (Found: Pt = 27·5 per cent.). The benzylamine filtrate was treated with ether when a dark brown precipitate came down. It was washed with ether, until it became granular, and was then washed successively with boiling alcohol (the alcoholic extract on standing deposited a yellowish-brown substance, which could not be sufficiently purified), benzene, acetone and finally with chloroform, until the washings were colourless. The residue was soluble in benzylamine from which it could be precipitated by ether. It is a brick-red powder (Found: Pt = 62·00; Cl = 5·34; N = 2·37. The presence of sulphur was proved. Pt_2Cl, $C_7H_7NH_2$, Et_2S requires Pt = 62·8; Cl = 5·6; N = 2·2 per cent.).

Action of Pyridine on PtCl, Et₂S.

PtCl, Et₂S and pyridine (excess) were heated on a water-bath for 2-3 hours. The solution was cooled and precipitated with excess of ether and filtered. The precipitate was washed repeatedly with ether and boiling alcohol and then repeatedly extracted with boiling benzene and filtered. The filtrate on cooling gave light yellow crystals, charring above 260.° (Found: Pt = 46·8; Cl = 16·29. PtCl₂, 2Py requires Pt = 46·24; Cl = 16·66 per cent.) The residue after extraction with benzene was boiled with chloroform to remove the unreacted original compound and filtered. The residue was insoluble in all solvents except pyridine, from which it could be precipitated by ether. (Found: Pt = 65·2; Cl = 6·3, N = 2·68; the presence of sulphur was proved. Pt₂Cl, C₅H₅N, Et₂S requires Pt = 65·8; Cl = 5·9; N = 2·34 per cent.)

Action of Piperidine on PtCl, Et₂S.

PtCl, Et₂S with excess of piperidine was heated on a water-bath for 3-4 hours. It was then filtered and washed twice with hot piperidine. The piperidine extract on addition of a large volume of ether and shaking gave a reddish brown granular precipitate, which was extracted repeatedly with boiling alcohol until the filtrate was colourless. It was then washed with boiling acetone, and subsequently dissolved in a minimum quantity of chloroform, filtered, and precipitated with ether. (Found: Pt = 60·3; Cl = 5·5; N = 4·34. The presence of sulphur was proved. Pt₂Cl, 2C₅H₁₁N, ½Et₂S requires Pt = 61·1; Cl = 5·0; N = 4·03 per cent.)

Action of Ethylamine on PtCl, Et₂S.

The platinum compound with excess of alcoholic ethylamine was kept for four hours in ice water in a

corked flask. The substance went into solution. It was then spontaneously concentrated when a crop of white crystals separated out, which were crystallised from boiling alcohol (Found: Pt $=43\cdot5$; Cl $=15\cdot3$. PtCl$_2$, 4EtNH$_2$ requires Pt $=43\cdot97$; Cl $=35\cdot84$ per cent.). The mother-liquor was evaporated to dryness in a vacuum desiccator and the residue extracted with warm water. The remaining residue was dissolved in alcohol and evaporated to dryness in a desiccator. The residue was again washed with alcohol when a small quantity of an undissolved compound was left behind. (Found : Pt $=69\cdot6$; Cl $=7\cdot00$; N $=2\cdot9$. Pt$_2$Cl, C$_2$H$_5$NH$_2$, Et$_2$S requires Pt $=69\cdot2$; Cl $=6\cdot3$; N $=2\cdot5$ per cent.).

Action of Pyridine on PtCl$_3$, 2Et$_2$S, 2H$_2$O.

PtCl$_3$, 2Et$_2$S, 2H$_2$O was added to an excess of pyridine, shaken well and somewhat concentrated by evaporation at the ordinary temperature. Water was added to the mixture and the solution filtered. The residue, a yellow crystalline product, was thoroughly washed with boiling alcohol and benzene. (Found : Pt $=40\cdot32$; Cl $=28\cdot18$; N $=5\cdot48$.. PtCl$_4$, 2C$_5$H$_5$N requires Et $=39\cdot63$; Cl $=28\cdot57$; N $=5\cdot63$ per cent.)

Action of Ethylamine on PtCl$_3$, 2Et$_2$S, 2$_2$HO.

To an alcoholic solution of the platinum compound an alcoholic solution of ethylamine was added when an orange precipitate was formed. The alcohol was removed by evaporation at the room temperature, the residue dissolved in water, filtered, and the filtrate concentrated in a vacuum over sulphuric acid. The first crop was obtained as pale yellow crystals in a quantity too small for analysis. The second crop consisted of orange

crystals. These were collected, washed with a small quantity of water and dried in a desiccator. (Found: $Pt = 42.32$; $Cl = 39.2$; N 6·06. $PtCl_5, 2C_2H_5NH_2$ requires $Pt = 42.41$; $Cl = 38.22$; $N = 6.03$ per cent.)

COLLEGE OF SCIENCE AND TECHNOLOGY,

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On the Nature of Hydrolytic Adsorption.

Part II.

Adsorption of Electrolytes by Barium Sulphate and Liberation of Acids and Alkalis in presence of Neutral Salts.

BY

for our observations. The difficulties in the way of alternative explanations have also been pointed out.

Experimental.

In this investigation indicators and standards recommended by Clarke and Lubs have been used. The standards have been tested in the laboratory. No filter paper was used as it is well-known that an acid reaction develops when filter papers are brought in contact with neutral electrolytes. The precipitate never came in contact with any surface other than that of the vessels (Jena glass or transparent fused silica) used. Washing was carried by repeated decantations.

(A) *Liberation of Adsorbed Acids and Bases by neutral Potassium Chloride.*

In these experiments 50 c. c. of a normal solution (p_H, 6·4) of barium chloride and of potassium sulphate (p_B 6·4) were added slowly and simultaneously from two burettes (the process taking 10—12 minutes) in a Jena glass bottle containing 25 c. c. of different acids (see Part I, *loc. cit.*, p. 199) regarding precipitation in presence of acids). The contents were kept undisturbed for 24 hours, and then the precipitate was washed repeatedly with pure water till the p_H of the wash-water left in contact with it for 24 hours had a value 6·2 to 6·4. The washed precipitate was next left in contact for 24 hours with 50 c. c. of saturated potassium chloride solution (p_H, 6·2—6·4). The results are given in Table I(*a*). Parallel experiments in which the precipitate obtained in an identical manner was kept in contact with water, instead of a solution of potassium chloride did not show a p_H value less than 5·8.

TABLE I (a).

Precipitated in presence of		p_H of the extract with KCl.
10N Hydrochloric acid	...	2·2
17N Acetic acid		2·4
8N Phosphoric acid		4·4
4N Citric acid		4·0
4N Tartaric acid		4·2
5N Sulphuric acid		2·2

TABLE I (b)

Precipitated in presence of N Sodium hydroxide		p_H of the extract.
	left in contact with sat. potassium chloride.	8·0
N· „ „ „	water	7·2

The same concentration of different acids was next used for comparison. The condition of experiments was identical with that in previous cases except that 50 c. c. of solution of acid were used. The results are given in Table II.

TABLE II.

Precipitated in presence of	p_H value of the KCl extract	
	after 24 hours	after 48 hours
N-Acetic acid	3·8—4·0	3·8
N-Monochloracetic acid	4·2	4·0
N-Dichloracetic acid	4·4	4·2
N-Trichloracetic acid	4·6	4·2—4·4
N-Hydrochloric acid	6·0—5·8	4·4
N-Formic acid	„	5·0
N-Phosphoric acid	„	5·4

	with KCl	with water	with KCl	with water
0·98N-Acetic acid	4·0	6·2	3·8	6·2
1·003N-Monochloracetic acid	4·2	6·2	4·0	6·2
0·98N-Trichloracetic acid	4·4—4·5	5·8	3·8—4·0	5·2—5·4
N-Hydrochloric acid	5·2—5·4	6·0	4·2	6·0

* The concentrations given are not exact and are meant to convey an idea of the strength of the acid that has been used.

Results of experiments with different concentrations of the same acid are given in Table III.

TABLE III (a).

Precipitated in presence of	p_H value of extract.
2·5N-Acetic acid	3·6
0·5N ,,	4·0
0·25N ,,	4·4
0·125N ,,	5·0
0·0625N ,,	5·6

TABLE III (b).

Precipitated in presence of	p_H value of extract.
0·5N-Sulphuric acid	3 8
0·25N- ,,	4·0
0·1N- ,,	4·2—4·4
0·05N- ,,	4 6

B. *Experiments with carefully washed Barium Sulphate precipitated in the absence of Acids.*

We see from the above that the concentration of the acid liberated in contact with potassium・chloride depends on the concentration and nature of the acid used. It was thought desirable to repeat the above experiments with barium sulphate precipitated in the absence of acids from neutral solutions of barium chloride and potassium sulphate.

Equal volumes (generally 50 c. c.) of normal solution of barium chloride and potassium sulphate were mixed

simultaneously from two burettes. The precipitate was washed repeatedly with pure water till the wash-liquid was free from sulphate and chloride. The precipitate was then kept in contact with an acid solution for 48 hours. It was again washed till the filtrate had a p_H equal to that of the water used (6·4). The precipitate was then left in contact with a saturated solution of potassium chloride (p_H, 6·4) for 24 hours and the p_H of the supernatant liquid was determined. It was observed that if the precipitate be washed sufficiently long no acid reaction develops on treatment with potassium chloride showing that the adsorbed acid can be removed more easily from these samples. On the other hand when the washing was not pushed far enough, definite evidence of the liberation of acids on treatment with potassium chloride was obtained as would appear from Table IV.

TABLE IV.

Kept in contact for 48 hours.	Washed free from acid and kept in contact with	p_H after 48 hours.
N-Oxalic acid	saturated potassium chloride (p_H, 6·2)	5·4
N-Oxalic acid	water (p_H, 6·2)	5·8
15N-Sulphuric acid	Saturated pot. chloride.	5·4
15N-Sulphuric acid	water	6·0

The observation that the precipitate does not develop an acid reaction if it is sufficiently washed also shows that the liberation of hydrogen ions is the result of an interaction between adsorbed acids and the neutral salt. In this respect the acidity developed here is different from that observed when hydrated silica or manganese oxides (cf. Part I, loc. cit., pp. 211, 215) is treated with a

solution of a neutral salt. Obviously barium sulphate cannot adsorb hydroxyl ions primarily to any perceptible extent as otherwise the acid reaction would be observed, however, long the washing may be continued.

It has been also observed that barium sulphate obtained from barium chloride and sulphuric acid and washed 'free from acid sets free chloride and sulphate ions in contact with neutral solutions of potassium nitrate and chloride respectively in addition, to hydrogen ions. But no barium ions could be detected. We have further observed that small quantities of the adsorbed ' acids are liberated in contact with pure water.

C. *Development of Alkalinity or Acidity from the double Decomposition of neutral Solutions of Potassium Chloride and Barium Sulphate.*

It has been stated previously (Part I., *loc. cit.*, p. 199) that an acid or an alkaline reaction develops on mixing neutral solution of potassium sulphate or barium chloride according as one or the other of the salts is in excess. The theoretical interest of this reaction is considerable.

(i) Development of Alkalinity when Barium Sulphate is precipitated from Excess of Potassium Sulphate.

Fifty c. c. of a normal barium chloride (p_H, 6·4) was added to 100 c. c. of normal potassium sulphate (p_H, 6·4) contained in a Jena-glass[1] bottle slowly as before but with constant stirring. The bottle was stoppered and shaken mechanically for 30 minutes and then allowed to stand. After half an hour the p_H value of the

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[1] This experiment as also the next one has been repeated in transparent fused silica vessels. No filter paper was used and the solution in these experiments never came in contact with anything other than Jena glass or silica vessels excepting that ordinary pipettes were used. It has been found that during the time for which the solution was in contact with the pipette no change in p_H value can be detected with the indicators.

clear supernatant liquid becomes 8·0. The p_H value exceeds 11·0 [1] in two to three days and remains steady afterwards.

(ii) Development of Acidity with Excess of Barium Chloride.

Fifty c.c. of normal potassium sulphate was added to 100 c.c. of normal barium chloride as before. The clear supernatant liquid (after 24 hours) does not show any acid reaction but remains neutral (p_H, 6·4). An acid reaction (p_H, 5·0) develops within 3 to 4 weeks. During this time the bottle was kept carefully stoppered in a place free from dust and fumes.

The immediate development of acidity and alkalinity can be demonstrated as follows:—

Two Jena glass test tubes are taken. To one of which are poured 5 drops of phenol red. One c.c. of barium chloride (normal solution) is next added. To the other tube are added 5 drops of methyl red and one c.c. of potassium sulphate (normal solution) and the liquid in both tubes is diluted to 4 c.c. Both the solutions are coloured yellow showing that the p_H, in each case is between 6·0—7·0. These tubes are kept in a holder for comparison. To another Jena glass test tube 2 c.c. of normal barium chloride (p_H, 6·4) 5 drops of methyl red and one c.c. of normal potassium sulphate are added and the solution is diluted to 4 c.c. A pink colour develops within 5 minutes showing on comparison with a phthalate standard a p_H value between 5·2 to 5·4.

To a fourth tube containing 2 c.c. of potassium sulphate and 5 drops of phenol red, 1 c.c. of barium chloride is added and the mixture diluted to 4 c.c. A red

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[1] Colour deep blue with thymolphthalein.

colour develops showing a p_H value on comparison with a phosphate standard between 8·0 to 8·2.

If the indicators are added after the precipitation that is, if the precipitation does not take place in the presence of the indicators as in the preceding experiments, a similar acid or alkaline reaction develops. These results have been confirmed by E. M. F. measurements.

Confirmation of the above Observation from E.M.F. Measurements.

Twenty-five c.c. of barium chloride having $p_H = 6·12$ (E. M. F. method—indicator showed p_H, 6·2) are mixed with 12·5 c.c. of potassium sulphate (pH, 6·0) and 12·5 c.c. of conductivity water (p_H, 6·4) in a conical Jena glass vessel and allowed to stand for 2 hours. The p_H of the upper liquid as determined by E. M. F. method is found to be 4·71. (The colorimetric method is not suitable on account of the presence of suspended particles which makes comparison with the standards difficult. Indicator showed a p_H value of about 5·0 as far as could be determined.) It has also been observed that the liquid above the precipitate gives an acid reaction either with indicator or with hydrogen electrodes so long as there are suspended particles in it. The decrease in acidity noted above is to be referred to a gradual clearing up of the supernatant liquid consequent on settling of suspended particles. It is also easy to understand why no acidity is observed in the upper liquid 24 hours after precipitation (see above) as by this time all the particles have settled and the liquid becomes perfectly clear. The precipitate, however, continues to give an acid reaction with methyl red. The fact that the clear supernatant liquid gradually develops acidity on further prolonged contact with the precipitate is obviously to be attributed

to a gradual diffusion of the acid from layers of liquid surrounding the solid particles. In this connection we would also like to record another interesting observation. When methyl red is added to freshly precipitated barium sulphate which has been prepared ,from equal volumes of barium chloride and sulphuric acid (normal concentration) and washed till no acid could be detected (with indicators and after 24 hours' contact with water) it takes up a yellow colour which does not change with time (up to 24 hours). An acid reaction (red colour) develops immediately on boiling or on the addition of a neutral solution of potassium chloride after some time. These observations have been repeated and confirmed.

Experiments were also carried out to see whether any acid or alkaline reaction develops when well washed barium sulphate precipitated from equivalent amounts of the reacting neutral salts are kept in contact with a solution of potassium sulphate or barium chloride or a mixture of potassium chloride and sulphate or potassium chloride and barium chloride in the preparation in which they occur in the above instances. No change in p_H was observed (indicators only have been used). It should be mentioned in this connection that when equivalent amounts of the two salts are used for precipitation the liquid either remains neutral (i. e., p_H remains practically unchanged) or develops slight alkalinity (p_H, 7·2—7·4).

Similar development of acidity or alkalinity can be shown if we take the nitrate of barium instead of the chloride and the ammonium or sodium salt in place of potassium sulphate.

(iii) *The Variation in the Alkalinity developed in presence of Excess of Potassium Sulphate with Time.*

We have already seen that the development of acidity or alkalinity takes time. It was, therefore, thought

desirable to follow the change in the alkaline reaction with time somewhat in detail. The stronger alkaline reaction makes it more easy to follow these changes.

Barium sulphate was precipitated with addition of 24 c.c. of normal barium chloride to 25 c.c. of normal potassium sulphate containing 0·01 equivalent of one of the following potassium salts—benzoate, citrate, bromide, salicylate, and of sodium chloride. It was found that a maximum p_H of 11·0 was observed in all cases but after 6 days, the p_H was found to be as follows :—benzoate (10·5), citrate (10·0), bromide (9·5), salicylate (9·0) and sodium chloride (8·0). The upper liquid becomes clear within a few hours after precipitation. Between 3 to 4 weeks each attains a steady p_H of 8·0. A parallel experiment without adding any external salt shows that after a p_H of 11·0 has been attained it diminishes more rapidly to 8·0 within 3 to 4 days. It was also found that with large excess of potassium sulphate there was no change in p_H after the maximum has been attained. The significance of these results will be discussed later.

(iv) Evidence as to the Separation of the Neutral Salt into Acid and Alkali.

Barium sulphate was precipitated with excess of potassium sulphate but the precipitate was washed very thoroughly till free from alkali as shown by the absence of an alkaline reaction after 24 hours. But when the precipitate is shaken with water vigorously the upper liquid shows a p_H of 3·8. Boiling the precipitate with water produces the above acidity very quickly.

When the precipitate is formed from excess of barium chloride, a cloudy suspension is formed on washing and it was not possible to wash it further,

D. *Electro-osmotic Experiments with Precipitated Barium Sulphate.*

From our point of view it is necessary to ascertain the sign of the charge of the precipitate in order to form an idea as to whether the hydrogen ions are coming from the primary or fixed layer of ions, or from the mobile sheet of the double layer. The apparatus is a modification of Brigg's method as used in this laboratory (*cf. Nature,* Dec. 2, 1922.) The results are qualitative. The rate of movement of the bubble is given in cms. per 3 minutes.

(i) *Dependence of the Sign of the charge carried by the Precipitate on the conditions of Precipitation.*

(*a*) We have already remarked that when precipitated from an excess of barium chloride by adding less than an equivalent amount of potassium sulphate the precipitate forms a colloidal suspension which is difficult to wash. On observing the direction of cataphoresis in a U-tube it is found that the particles are *positively* charged. This observation has been repeated several times and there is no doubt that the particles precipitated from an excess of barium chloride carry a positive charge. If the liquid is decanted as far as possible and pure water is added to the precipitate the suspension that is formed also contains positively charged particles showing that the partial removal of the electrolytes does not change the sign of the charge.

(*b*) On the other hand the precipitate from an excess of potassium sulphate has no tendency to pass into the colloidal state on washing and the direction of electro-osmosis is with the positive current showing that the liquid in contact with the particles is positively charged and that the particles carry a negative charge. The

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precipitate is previously washed free from sulphate before it is used for electro-osmotic experiments.

(c) When the precipitate is formed by mixing equal volumes of normal solutions of potassium sulphate and barium chloride and is washed free from chloride the direction of electro-osmotic flow shows that the particles carry a slight negative charge. We could not observe a positive charge though we repeated the experiments three times.

(d) When precipitated from equal volumes of normal solutions of sulphuric acid and barium chloride. and washed free from acid the particles carry a definite *positive* charge.

(ii) *Variation in the Charge on the Addition of Electrolytes.*

In these experiments the precipitate was obtained from mixing large volumes of hot dilute solutions of potassium sulphate and barium chloride using a very small excess of the sulphate. The precipitate was washed free from sulphate with hot water. (70°—80°). The variations in the charge of the particles in contact with barium chloride and sulphuric acid have been investigated. The data are given below :

Electrolyte.	Concentration	Rate of movement in cms. per 3 min.s	Sign of charge.
Barium chloride	0 (water)	4·3	Negative
	0·0002 N	3·9	,,
	0·0004 N	42	Positive
	0·001 N	10·2	,,
Sulphuric acid	0 (water)	5·5	Negative
,,	0·002 N	7·2	,,

Discussion.

It will be convenient to discuss the results under two heads as follows.

A'. *Generation of Acids and Alkalis by double Decomposition of Neutral Solutions of Potassium Sulphate and Barium Chloride.*

The adsorption of electrolytes by barium sulphate during precipitation is well known (*cf.* Treadwell-Hall, "Analytical Chemistry," Vol. II, 1924, pp. 401-5; Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. III, *19*, pp. 765-6, where references to literature are given). Hulett and Duschak (*Z. anorg. Chem.*, 1904, *40*, 196) assume the existence of such salts as $BaClHSO_4$; $(BaCl)_2 SO_4$ and $Ba(HSO_4)_2$ in the precipitate, Similar salts are also well-known. Whenever explanations based on chemical reactions are put forth the question as to the nature of the solid phase arises.

Are we to regard the solid as a mixture of two or more pure solid phases or as a mixture of solid phases one of which is a solid solution? Further, what is the part played by the solid-liquid interface in these reactions? We have already seen that compounds of barium sulphate with acids are known. Apart from the question of stability of such salts under the conditions of precipitation their formation in minute quantities can explain the development of alkalinity. But so far as we know compounds of barium sulphate with hydroxides of alkali or alkaline earth metals are unknown and it is difficult to account for the generation of acidity on the assumption of the formation of definite chemical compounds.

Besides from the orthodox chemical point of view the relationship between the charge carried by the particles and the chemical reaction which we have observed

is not contemplated. Two alternative explanations may be suggested based respectively (*a*) on the adsorption of ions and the nature of the electrical double layer surrounding the colloidal particles, and (*b*) on Donnan's well known conception of equilibrium between ions across membranes. In either case it is assumed that when precipitated from excess of barium chloride the particle has an excess of barium ion adsorbed on the surface, and an excess of sulphate ion when precipitated from excess of sulphate. The particles consequently would carry respectively positive and negative charges. Taking the case when barium chloride is in excess if we assume that the precipitate appears in the form of fine particles forming a sort of membrane and that the ' membrane ' structure, in places completely encloses the liquid like a sac it is possible to imagine that the liquid enclosed in the sac has a higher concentration of barium chloride than what obtains in the bulk of the liquid outside it. In that event diffusion of barium chloride will set in from inside the sac towards the exterior. On account of the positive charge carried by the membrane the diffusion of the barium ion through it will be slower than that of the chlorine ion with the result that acid will appear outside and alkali inside the sac. Similarly we can account for the alkalinity when the sulphate is in excess. The assumption of a diminution of the rate of diffusion when the membrane has a charge of the same sign is not new. Fischer (*Koll. Zeitsch* 1920, *30*, 13) made such an assumption with a view to explain the formation of Liesegang rings on the basis of Bradford's suggestion (*Biochem. J.*, 1916, *10*, 167) that the adsorption of constituent ions is in part responsible for the formation of such rings. From the above point of view it would follow that the difference in concentration of barium chloride inside and outside the sac as also the magnitude

of the positive charge will determine the degree of acidity developed. If instead of using barium chloride and potassium sulphate of the same concentration, a higher concentration of barium chloride is used in the precipitation, one would expect that in the initial stages of precipitation the difference in the concentration of barium chloride inside and outside will be increased. Further higher concentrations of barium chloride may also increase the positive charge and thus decrease the rate of diffusion of barium ion still further. But experiments on these lines show the absence of any such effects. There is no material change in the acidity. Moreover, this explanation is based on a number of assumptions of which one cannot be very sure. For instance under the conditions of precipitation it is not very likely that there will be a difference in the concentration of barium chloride to any marked degree. On the other hand a much simpler explanation is possible. From our point of view, we can form the following picture of the double layer. Ordinarily the surface of a pure crystal of barium sulphate consists of barium and sulphate ions spaced in conformity with its crystal structure. When there is an excess of barium chloride present in the solution, some of the barium ions become fixed in close proximity to the sulphate ions and the surface has more barium ions per unit area than otherwise. In this case, there is a probability of a partial displacement of the chlorine ions which are present in the mobile sheet by hydroxyl ions on account of the greater adsorbability of the latter. It is well-known that the effect of hydrogen and hydroxyl ions respectively on negatively and positively charged colloidal surfaces are decidedly greater than that of most other inorganic cations and anions respectively. Some of the chlorine ions of the mobile sheet may be displaced by the hydroxyl ions of water and the displaced chlorine ion

together with the partner hydrogen ion of the hydroxyl ion will maintain the electrical neutrality of the solution. The extent of the replacement will be actually determined by the relative adsorbabilities and concentrations of the two ions. Though the adsorbability of hydroxyl ions ·is very great its concentration is very small, and only· when we have a large development of specific surface and consequently a large solid-liquid interface the effect will be measurable. The · sensitiveness of ₐthe ₐmethods for determining hydrogen ion concentrations makes it relatively easy to observe such effects. We thus see that the amount of acid liberated depends on the following factors—(1) number of barium ions remaining adsorbed at any instant under consideration, (2) relative adsorba-, bility of chlorine' and hydroxyl ions, and (3) their relative concentrations. The extent of adsorption of the barium ion depends (a) on the number of places on.the surface where it can be adsorbed, (b) the intensity of its adsorption, and (c) its concentration in the solution. The particles, are thus coated with ₑ molecules of barium hydroxide at places and the liberated acid gradually diffuses away from the surface and on account 'of the slowness of the process of diffusion and the small amount of acid liberated, the acidity can only be observed at first on adding an indicator to the precipitate itself or when, the particles themselves remain suspended in the solution. In time sufficient acid diffuses into the bulk of the liquid to give a measurable effect.

The greater and more rapid development of alkalinity probably indicates either (i) a more. intense adsorption of sulphate ions on the surface or (ii) a greater difference between adsorbabilities of hydrogen and potassium ions, than between chlorine and hydrogen ions. Further work is necessary 'before we can be sure of the case of this difference. We shall see in next section that

hydrogen ions are probably fixed on SO''_4 ion forming HSO'_4 ions.

(B) Liberation of Adsorbed Acids and Alkalis by Neutral Salt Solutions.

It has already been stated that compounds between acids and barium sulphate are well-known and that during precipitation, formation of such salts in minute traces has been suggested by several investigators. Formation of complex acids containing barium sulphate cannot account for the positive charge of the surface when the salt is precipitate in the presence of acids or the increase in the negative charge with dilute solution of sulphuric acid observed with barium sulphate precipitated from neutral solutions. That the particles are charged positively shows that we are not dealing with neutral molecules of complex acids present either at the surface or distributed, throughout the entire mass but that there is an excess of ions of one kind on the surface. When precipitated in presence of high concentrations of acids the hydrogen ions are primarily adsorbed by the surface and impart a positive charge to it. Strong adsorption of hydrogen ions clearly points to the formation of HSO'_4 ions, the corresponding anion remains mobile in the double layer. On washing the HSO'_4 ions on the surface slowly break down and liberate acids. The stability of the HSO_4 ions so far as it depends on electrostatic forces can be ascribed to the small diameter of hydrogen ion and the double charge of the SO''_4 ion. On addition of a neutral electrolyte partial replacement of hydrogen ion in the HSO'_4 ion by K' ion takes place on account of the high concentration of the latter and KSO'_4 ions are formed. The HSO'_4 ions are stable only in presence of high concentrations of acids. The interchange of K' and H' ions takes place in the fixed

layer of ions and the process will be slower than what would have been the case if we were dealing with an interchange of ions in the solution with those in the mobile layer. Besides the diffusion of the liberated acid from the surface is slow. The gradual increase in acidity of the solution should be ascribed to these factors. On the other hand the electro-osmtic experiments with salts precipitated from neutral solutions and treated subsequently with acids show that the hydrogen ions come from the mobile layer. We have seen that the particles initially carry a negative charge which increases still further at low concentrations of sulphuric acid. Under these conditions more sulphate ions are adsorbed on the surface than the H' ions and the latter constitute the mobile layer.

Taking the evidence as a whole we believe that at low concentrations of sulphuric acid the adsorption of sulphate ions predominates over that of hydrogen ions the reverse of which takes place at high concentrations. In concluding the discussion we would point out that the simultaneous measurement of the charge carried by the particles gives a clear idea of the nature of the reaction.

Studies on the Dependence of Optical Activity on Chemical Constitution. Part VII. Stereoisomeric Aryl Derivatives of Imino- and Bisimino-Camphor and their Absorptive Spectra.

BY

Bawa Kartar Singh

AND

Raghunath Rai.

Stereoisomerism of the Hantzsch-Werner type in hydrazones, semicarbazones and phenylcarbamylhydrazones of camphorquinone has been definitely established (Forster and Zimmerli, *J. Chem. Soc.*, 1910, 97, 2156), and their α and β forms are regarded as anti- and syn-carbonylic respectively :

$$C_8H_{14} < \begin{array}{c} C=N-NHX \\ CO \end{array} \qquad C_8H_{14} < \begin{array}{cc} C=N \\ CO & NHX \end{array}$$
$$(\alpha) \qquad\qquad (\beta)$$
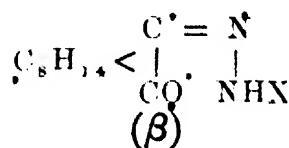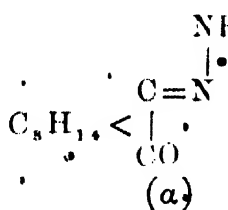
Iminocamphor and its aryl derivatives which contain an azethenoid group should also be capable of existing in two stereoisomeric forms (I) and (II) :

$$C_8H_{14} < \begin{array}{c} C=N-R(H) \\ CO \end{array} \qquad C_8H_{14} < \begin{array}{cc} C=N \\ CO & R(H) \end{array}$$
$$(I) \qquad\qquad (II)$$
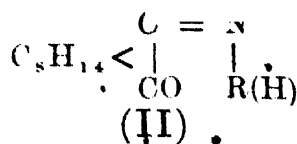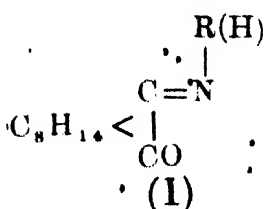
The difficulty of eliminating structural isomerism in the case of the hydrazones, semicarbazones, etc., alluded

to by Forster and Zimmerli (*loc. cit.*), which is due to the presence of the hydrogen atom in the -NHX group, linked to nitrogen of the azethenoid group, is, however, absent in the aryl derivatives of imino- and bisimino-camphor. It would, therefore, seem to be easy to establish the existence of the Hantzsch-Werner type of stereoisomerism in these classes of compounds. Notwithstanding this, numerous derivatives of iminocamphor have been obtained in one form only (Forster and Thornley, *J. Chem. Soc.*, 1909, *95*, 944; Singh and collaborators, *J. Chem. Soc.*, 1919, *115*, 566; 1920, *117*, 980, 1599), except in the case of 4-hydroxy-*a*- naphyl-imino-camphor, which exists in two forms (unpublished work). The case is different with the derivatives of bisimino-camphor. *p:p'*- Diphenylene- and *o:o'*- ditolylene-bisimino-camphor have been shown by one of us to exist in two forms (Singh, Singh, and Lal, J. *Chem. Soc.*, 1921, *119*, 1971). " They may be represented by two out of three possible stereo-chemical configurations, (III), (IV) and (V), which are designated as *anti-*, *syn-*, and *amphi-* carbonylic respectively :

(III) *anti*   (IV) *Syn*

R = H OR CH

(V) *amphi*
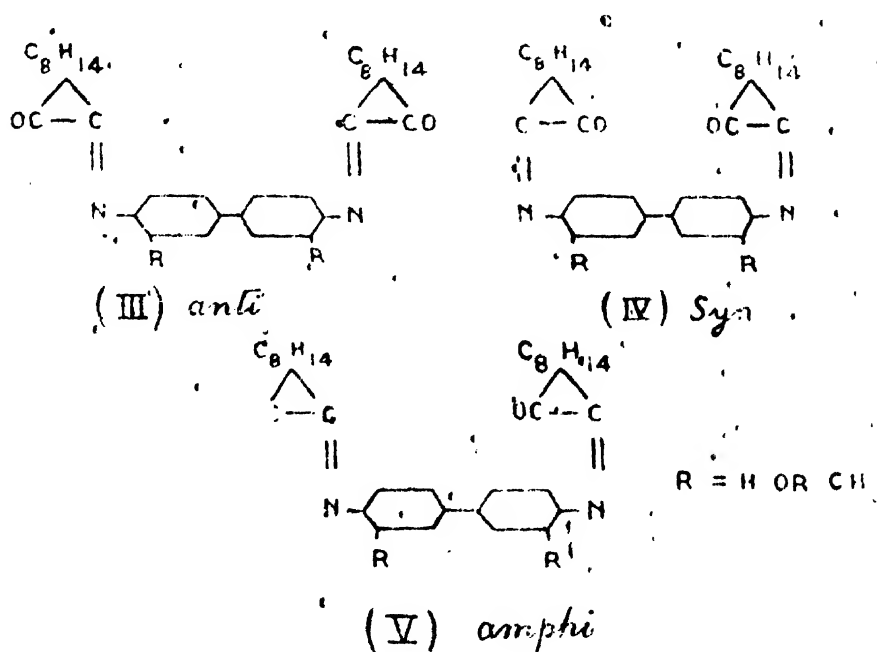
If this view is correct, then on reduction, (III), (IV) and (V) should each furnish the same bisaminocamphor derivative* (VI):

$$C_8H_{14} \left\langle \begin{array}{c} \overset{*}{CH} \cdot NH \\ | \\ CO \end{array} \right. \text{—} \bigcirc\text{—}\bigcirc\text{—} \left. NH \cdot \overset{*}{CH} \atop OC \right\rangle C_8H_{14}$$

$$\quad R \quad\quad R$$

(VI.)
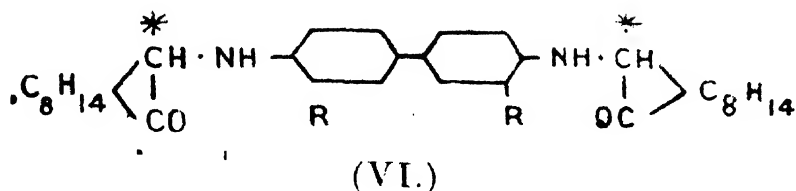
In conformity with this view it was found (*loc. cit.*) that *p:p′*-diphenylenebisamino-camphor was produced by the reduction of both the forms. This result disposes of structural isomerism of any kind, and, in conjunction with experiments on the mutual interconversion of the two forms of 4-hydroxy-α-naphthyliminocamphor by the action of solvents and heat, appears to us to establish incontestably that stereoisomerism of the Hantzsch-Werner type exists.

There is no chemical method available by which the configurations of these isomers may be allocated.' The only point of attack by chemical means is the carbonyl group in the β-position of the *camphane* molecule, but its indifferent reactivity, which is familiar, does not lend itself to chemical transformations. It was, therefore, thought desirable to determine the absorption spectra of these and other similarly constituted compounds with a view to correlate them with their optical rotatory power. It is well known that unsaturation increases general

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*As two new carbon atoms (marked with an asterisk) are rendered asymmetric, the optically active compounds having the configurations (III), (IV) and (V) can each yield theoretically on reduction the same three stereochemical isomers αα, ββ, αβ, represented by the structural formula (VI) In practice, however, only one and the same of these isomers was produced from both the forms.

absorption, and that among the unsaturated compounds the *trans-* or *anti-* variety is more absorptive than the *cis-* or *syn-*(Stewart, *J. Chem. Soc.*, 1907, *91*, 199; compare also Magini, *Atti R. Accad. Lincei.* 1903, (V), *12*, ii, 29; *J. Chim. Phys.*, 1904, 2, 410). A relation between absorptive and optical rotatory power of unsaturated compounds which has been developed by Stewart (*loc. cit.*) into the rule "greater absorption, greater rotation" may be expanded into the generalisation that the *trans* or *anti* variety has greater rotation and greater absorption than the *cis* or *syn*. It was therefore hoped that as a result of the correlation of the optical rotatory power and absorption spectra of these isomers, their stereochemical configurations may be deduced. Though the attempt cannot be said to be entirely successful, some interesting results have emerged from this work.

In Fig. I, the absorption spectra curves of the two forms of *p:p'*-diphenylene- and *o:o'*-ditolylene-bisiminocamphor, together with those of the *o:o'*-dimethoxydiphenylene derivative in chloroform solution are given. It is seen that these compounds exhibit general absorption. The data with regard to these compounds (*loc. cit.*) may be conveniently summarised here:

TABLE I.

p:p'-Diphenylenebisiminocamphor.

	Colour.	m.p.	Solubility.	$[M]_D$	Absorption.
1.	Golden-brown	274°	more	5432°($CHCl_3$)	more
2.	Green	276°	less	5472 „	less

Fig. I

FREQUENCIES

LOG OF THICKNESSES ($\frac{N}{10,000}$ solution).
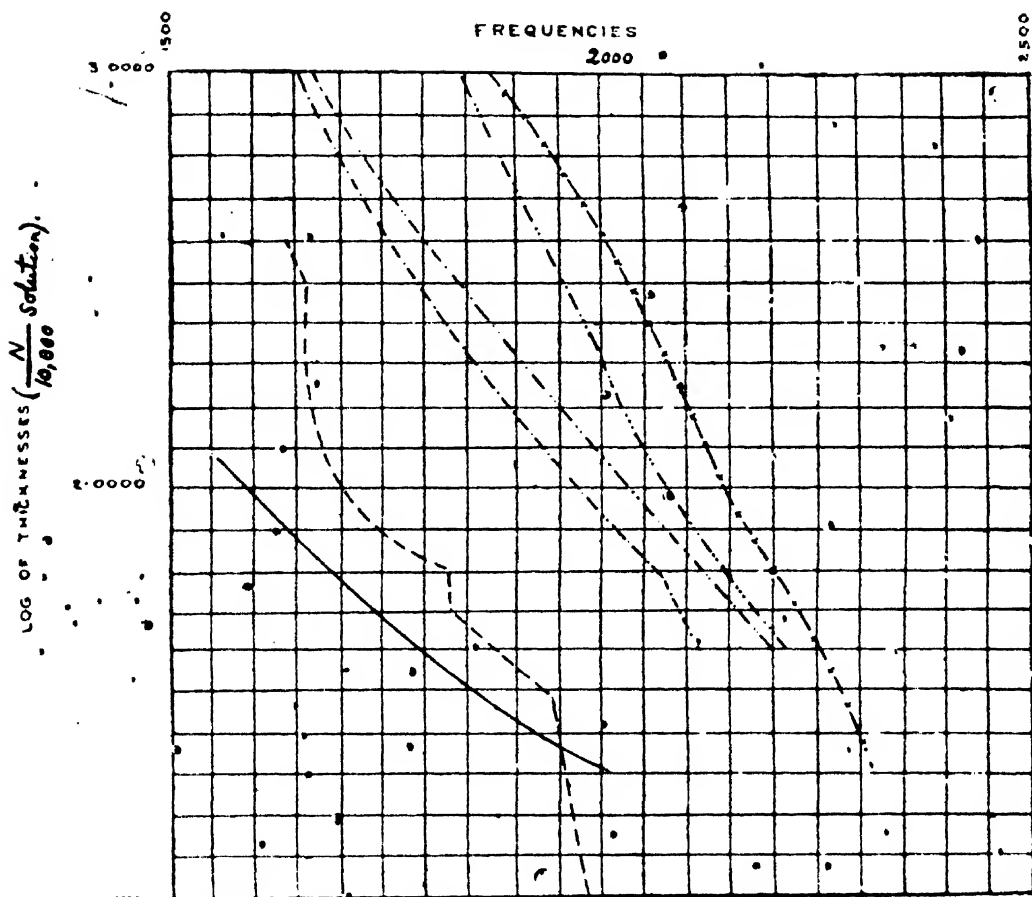
— ×—p : p-DIPHENYLENE-BIS-IMINOCAMPHOR (GREEN VARIETY).
— · · —p : p-DIPHENYLENE-BIS-IMINOCAMPHOR (RED VARIETY).
— · · · —p : p-DITOLYLENE-BIS-IMINOCAMPHOR (GREEN VARIETY).
— · —p : p-DITOLYLENE-BIS-IMINOCAMPHOR (GOLDEN YELLOW VAR:).
— · — —p : p-DIMETHOXY-DIPHENYLENE-BIS-IMINOCAMPHOR.
————p : p-DIMETHOXY-DIPHENYLENE-BIS-IMINOCAMPHOR.
(AFTER THE SOLUTION HAD BEEN KEPT FOR A WEEK).

o:o′-Ditolylenebisiminocamphor.

	Colour	m.p.	Solubility	$[M]_D$	Absorption
1.	Yellow	198–199°	more	4007°(CHCl₃)	more
				3462 (CH₃OH)	
2.	Green	200–201°	less	3929 (CHCl₃)	less
				3274 (CH₃OH)	

The yellow variety of o:o′-ditolylenebisiminocamphor which is more absorptive than the green variety (as its curve lies at lower frequencies) possesses higher rotatory power, and this is in harmony with Stewart's rule (loc. cit.) It may, therefore, be represented by trans or anti configuration (III). The case is, however, different with p:p′-diphenylenebisiminocamphor where the more absorptive form has lower rotatory power. It is, however, to be noticed that the difference in the rotatory powers of the two forms, in this case, is very small.

The application of the relation between optical rotatory power and configuration, as deduced from a study of the hydrazones, semicarbazones and phenylcarbamyl hydrazones of Forster and Zimmerli (loc. cit.) leads to the same result. The a-derivatives which are regarded as anti-carbonylic have higher molecular rotation. In other words, the higher rotatory power is associated with anti or trans-configuration. The o:o′-ditolylene derivative which has higher rotatory power would be regarded as anti, and should, therefore, be more absorptive. This is found to be the case. The p:p′-diphenylene derivative which has higher rotatory power would likewise be represented by anti configuration. It should, therefore, be more absorptive but it is less. The uncertainty caused by the existence of a third configuration in the bisimino-camphor derivatives is not to be overlooked, and we are not sure which two pairs are being compared. This may

explain the anomalous results in the case of the diphenylene derivatives.

In Fig. II, the absorptive spectra curves of six compounds in chloroform solution are plotted. These compounds, which naturally fall in two series, also exhibit general absorption. The relation between rotatory power, absorptive power, and unsaturation is brought out very clearly by counting the number of double linkings in the structural formulae of these compounds (Tables II and III), and comparing the molecular rotatory powers and absorption spectra curves in chloroform :

TABLE II.

m-Phenylene-bisimino-camphor.

$$C_8H_{14} \left\langle \begin{array}{l} C=N- \\ | \\ C=O \end{array} \right. \quad \bigcirc \quad \left. \begin{array}{l} N=C \\ | \\ O=C \end{array} \right\rangle C_8H_{14} \quad 2660°$$
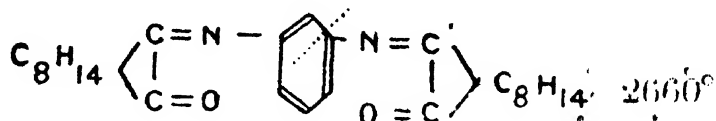
7 double linkings,
    but conjugation broken
    at dotted line.

p-Phenylene-bisimino-camphor.

$$C_8H_{14} \left\langle \begin{array}{l} C=N- \\ | \\ C=O \end{array} \right. \quad \bigcirc \quad \left. \begin{array}{l} N=C \\ | \\ O=C \end{array} \right\rangle C_8H_{14} \quad 6088$$
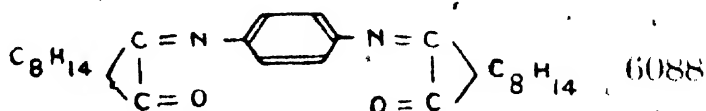
7-double linkings,
    conjugation complete.

1 : 4-Naphthylene-bisiminocamphor.

$$C_8H_{14} \left\langle \begin{array}{l} C=N- \\ | \\ C=O \end{array} \right. \quad \bigcirc\!\!\bigcirc \quad \left. \begin{array}{l} N=C \\ | \\ O=C \end{array} \right\rangle C_8H_{14} \quad 8157$$
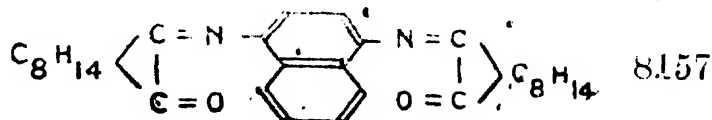
9-double linkings,
    conjugation complete.

FIG. II
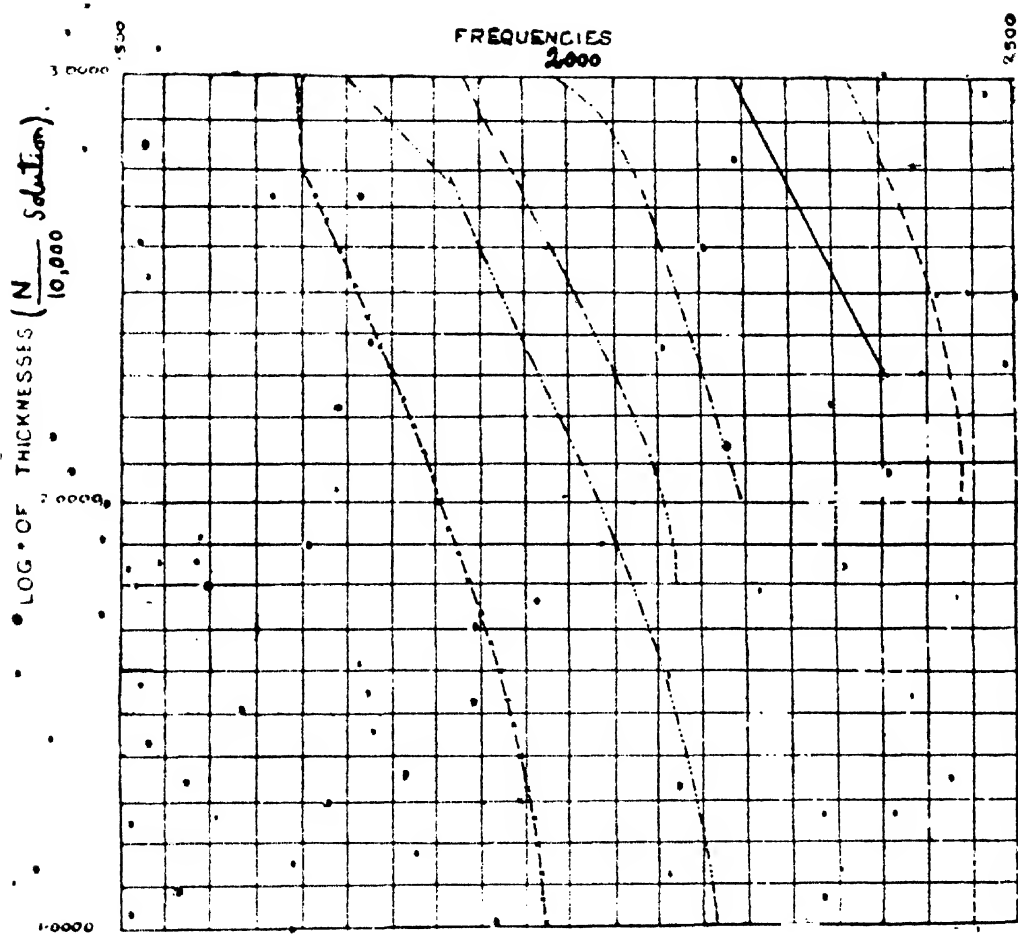
──── PHENYL-IMINOCAMPHOR.

─··─ m-PHENYL-BIS-IMINOCAMPHOR.

─·· ─ p-PHENYLENE-BIS-IMINOCAMPHOR.

─···─ α-NAPHTHYL-IMINOCAMPHOR.

─··─ α-NAPHTHOL-IMINOCAMPHOR (OR, P-HYDROXY-α-NAPHTHYL-IMINOCAMPHOR.)

──×── 1:4-NAPHTHYLENE-BIS-IMINOCAMPHOR.

TABLE III.

Phenyliminocamphor. C_8H_{14} < $\begin{matrix} C=N- \\ | \\ C=O \end{matrix}$ ⬡   1750°

5 double linkings.

α-Naphthylimino-camphor. C_8H_{14} < $\begin{matrix} C=N- \\ | \\ C=O \end{matrix}$ ⬡⬡   1774°

7 double linkings.

4-Hydroxy α-naphthyliminocam-phor. C_8H_{14} < $\begin{matrix} C=N- \\ | \\ C=O \end{matrix}$ ⬡⬡—OH

yellow form, 3991°

orange form, 3948°

7 double linkings.

This survey shows clearly that the compounds which possess the greater number of unsaturated conjugated linkages have greater absorption as well as greater rotation. In other words, the rotatory power and the absorptive power are similarly affected by unsaturation.

4-Hydroxy-α-naphthyliminocamphor (unpublished yet) exists in two modifications, orange and yellow, which are undoubtedly stereoisomeric of the type under discussion. They, however, give an identical absorption spectrum curve (Fig. II), which is that of the equilibrium mixture of the two varieties in solution. This view receives support from observations on mutarotation in methyl alcohol; the value of $[M]_D$ for the yellow form

is 5070° (after six minutes), 4095° (3½ hours), and   3733°
(27 hours); that for the orange variety to 3516° (⅓ hour).
The values of $[M]_D$ in chloroform (Table III) are practi-
cally identical and refer to those of the equilibrium
mixture of the two forms.   This is confirmed by the
direct transformation of the yellow forms into the orange
in these solvents.   The reverse change is brought about
by heat.

The Manufacture of Strychnine and Brucine from Nux Vomica.

BY

E. R. WATSON AND H. D. SEN.

When a process comes to be considered on a large scale many factors have to be considered which are usually neglected when the operations are carried out in the laboratory, such as cost of reagents, steam, and labour and initial cost of plant. For this reason the following experiments on the extraction of strychnine and brucine from *nux vomica* on a semi-large scale may be of interest.

Several processes are described in a general way in the literature. The first process tried was the extraction by dilute alcohol, evaporating off the alcohol, precipitating tannin by lead acetate and finally precipitating crude alkaloid from the filtrate by alkali. This process gave very impure alkaloid. The next process tried was one generally employed in alkaloid extraction, *viz.*, making the material alkaline and extracting with some solvent immiscible with water such as toluene or kerosene oil. The prescription used at the Government Cinchona Factory, Bengal, for the manufacture of quinine from cinchona bark was tried. This consists in mixing the material with lime and caustic soda and water and extracting with hot kerosene oil. This proved unsatisfactory as the aqueous mixture and the kerosene oil formed an obstinate emulsion.

The process was modified by mixing the powdered *nux vomica* with lime and water, drying, powdering and

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extracting with hot kerosene oil. This gave a satisfactory result, but on a large scale the drying of the material is one of the most expensive parts of the process, both as regards steam and initial cost of plant. Experiments were therefore made by steaming the nuts to soften them, mixing with lime and passing through a disintegrator and extracting with hot kerosene without previous drying. This also gave a satisfactory result and the process as finally worked out was as follows.

A half-maund (41 lbs.) *nux vomica* (whole nuts) was heated in an autoclave with $1\frac{1}{4}$ times its weight of water at 30 lbs. pressure for 3 hours. Thirteen pounds of quick-lime were slaked with the surplus water from the autoclave and a little additional water until it fell to a powder. The steamed nuts were mixed with the lime and passed through the disintegrator. This material was extracted with 20 gallons kerosene at 90° in a closed pan for 1 hour with vigorous stirring and then the kerosene was separated from the mud by passing through a centrifuge. The kerosene oil was extracted with 40 lbs. dilute acid (containing 372g. sulphuric acid (D 1·84)) in a lead lined pan at 90° for 1 hour with stirring. The acid layer was run off, filtered and neutralised with a solution of 500 g. soda ash in 5 lbs. water. After standing overnight a first crop of 265 g. of alkaloid was filtered off. The mother-liquor was concentrated to one quarter of its bulk and gave a further precipitate of 93 g. of alkaloid. The alkaloid was dried in the steam-oven and extracted with its own weight of cold acetone. The residue insoluble in acetone was dissolved in hot dilute sulphuric acid and on cooling a crop of strychnine sulphate was deposited. On concentrating the mother-liquor a further crop of strychnine sulphate was obtained. On the average 6 ozs. of strychnine sulphate were obtained, but in some experiments the yield was more than this. The strych-

nine sulphate was free from brucine. It was purified by recrystallisation from hot water. In these operations there was a loss of 2 gallons kerosene oil and of acetone equal to the weight of alkaloids treated.

The following is an estimate of the daily working expenses in handling 25 maunds *nux vomica* in a properly designed plant at Cawnpore.

	Rs.	As.
25 mds. *nux vomica* at Rs. 4-8 in Calcutta	112	8
Freight on same to Cawnpore at Rs. 2 per md.	50	0
Bags for same at as. 4 per maund ...	6	4
Carting in Calcutta and Cawnpore ...	4	0
Coal	17	0
Lime at Re. 1 per maund	8	4
Sulphuric acid (D. 1·75 at as. 2 per lb. Cawnpore)	6	0
Soda ash at Rs. 10-8 per cwt. (Cawnpore price)	5	4
Labour and mistri	12	8
25 tins kerosene oil at Rs. 3-12 ...	93	12
30 lbs. acetone at Rs. 1-8... ...	45	0
Total	360	8

The value of the product may be estimated as:—

18¾ lbs. strychnine sulphate at Rs. 1-10 per oz. (London price) or Rs. 22 per lb. Rs. 409·8.

In this process it is necessary to have efficient stirring during the extraction with hot kerosene; otherwise the whole of the alkaloid is not extracted in one operation and a second extraction is necessary with increase in working charges.

Experiments have shown that the process can be further simplified by omitting the precipitation of alkaloids by soda and simply concentrating the acid-liquor, which has extracted the alkaloids from the kerosene,

when strychnine sulphate crystallises out. In this case the sulphuric acid must be cut down to 240 g. (D 1·84)., From half-a-maund there was obtained 6·8 oz. strychnine sulphate free from brucine.

The recovery of pure brucine from the remaining alkaloid has not yet been worked out fully. The crude brucine extracted by cold acetone from the total alkaloids can be crystallised from 25 per cent. alcohol (decolourising with a little animal charcoal) and obtained in a pure condition.

The *nux vomica* used in these experiments contained 2·6 per cent. of total alkaloids.

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Synthesis in the Iminazole series:
Some derivatives of Isiminazole.

BY

PRAFULLA CHANDRA MITTER AND NRIPENDRA NATH SINHA.

The iminazole group contains many substances which are formed in the metabolic processes of the living organism. Among these oxo-derivatives like hydantoin, allantoin and parabanic acid are of special importance. While the 2-4-di-oxo-derivatives are largely represented only a few 4-5-di-oxo-derivatives are known. The synthesis of parabanic acid from urea and oxalyl chloride (Biltz and Topp, *Ber.*, 1913, *46*, 1387), and of *o*-methyl *iso*-parabanic acid from *o*-methyl *iso*-urea and oxalic ester (Bruce, *Amer. Chem. J.* 1904, *26*, 456) led us to investigate the action of oxalyl chloride, oxalic ester and oxaminic ester on amidines. With benzamidine and *p*-toluamidine dioxo-dihydro-iminazoles are easily obtained. With acetamidine however, our labours have, so far, not been attended with success, due probably to the great instability of acetamidine (Pinner: "Die Imidoether," p. 107).

From the dioxo-compounds the oxo-chloro derivatives may be easily obtained by the action of phosphorus oxychloride.

It is interesting to note that the oxo-chloro-compounds may be regarded as representatives of the hitherto unknown group of *isiminazoles*.

EXPERIMENTAL.

2-*Phenyl-4:5-dioxo-4:5-dihydro-iminazole.*

$$C_6H_5C \diagdown \begin{matrix} NH - CO \\ | \\ N - CO \end{matrix}$$
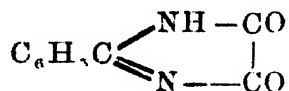
(1) From oxalic ester and benzamidine.

Potassium hydroxide (1·12g.) dissolved in water (5 c.c.) was added to benzamidine hydrochloride (3 g.) dissolved in water (10 c. c.) in a stoppered bottle. Then oxalic ester (3 c. c.) was quickly added. Heat was generated and an intense yellow colour developed. The bottle was cooled and the yellow colour gradually faded. The mixture was allowed to stand for three or four days with occasional shaking. The solid product was collected, washed with water and recrystallised from alcohol.

It is soluble in water, alcohol and glacial acetic acid, insoluble in ether and acetone; m. p. 174° with decomposition. (Found: $N = 15·82$. $C_9H_6O_2N_2$ requires $N = 16·09$ per cent.).

(2) From oxalyl chloride and benzamidine.

Benzamidine was liberated from the hydrochloride by means of concentrated potassium hydroxide solution. The free base was extracted by ether and a little more than the calculated quantity of oxalyl chloride was added drop by drop, with constant stirring. After about an hour the ether was evaporated by keeping it in a vacuum desiccator and the residue crystallised from alcohol. It was identical with the substance already obtained, (Found: $N = 15·77$).

2-*Phenyl-4-chloro-5-oxo-isiminazole.*

Freshly distilled phosphorus oxychloride (5 c.c.) was added to the dioxo compound (5 g.) in a flask fitted with

a condenser. The mixture was heated on the water-bath for fifteen minutes and then poured on a small quantity of crushed ice. The solution was nearly neutralised with sodium carbonate, evaporated to dryness and extracted with absolute alcohol. On concentrating the solution, the chloro compound separated in shining needles, m.p. 215° with decomposition. It is very soluble in water, and alcohol, insoluble in ether and benzene. (Found : Cl = 18·41. $C_9H_5ON_3Cl$ requires Cl = 18·44 per cent.).

2-p-*Tolyl-4-5-dioxo-dihydro-iminazole.*

(1) From oxalic ester and p-toluamidine.

p-Toluamidine hydrochloride (3·4 g.) potassium hydroxide (1·12 g.) and oxalic ester (3 c.c.) were treated in the same manner as in the case of benzamidine. After standing overnight the solid product was crystallised from a large quantity of boiling water. It does not melt up to 280°.

It is soluble in hot water, warm alcohol, acetic acid and hydrochloric acid, insoluble in acetone and benzene. (Found : N = 14·68. $C_{10}H_8O_2N_2$ requires N = 14·88 per cent.).

(2) From oxalyl chloride and p-toluamidine.

The procedure was the same as in the case of benzamidine. (Found : N = 14·71 per cent.).

(3) From oxaminic ester and p-toluamidine.

Oxaminic ester (2·1 g.) was added to a dry ethereal solution of p-toluamidine liberated from the hydrochloride (5 g.) and the mixture was well-shaken. The odour of ammonia was distinctly perceptible. The mixture was allowed to stand for a day and the solid product was recrystallised from alcohol. The substance was found to be identical with the product obtained with oxalic ester or oxalyl chloride. (Found : N = 14·73 per cent.).

2-p-Tolyl-4-chloro-5-oxo-isiminazole.

$$CH_3.C_6H_4.C \diagup \begin{matrix} N=C.Cl \\ | \\ N-CO \end{matrix}$$
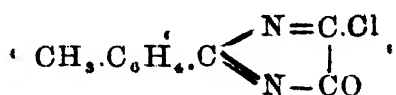
The dioxo compound (5 g.) was heated with phosphorus oxychloride (5 c.c.) on the water-bath for about fifteen minutes and then poured over a small quantity of crushed ice. The hydrochloride separated in the form of crystals. It was filtered and dissolved in a small quantity of water and poured into a concentrated solution of sodium acetate. The crystalline precipitate was filtered and dried and crystallised from a mixture of alcohol and ether. The substance sublimes between 260 and 265°.

It is very soluble in water, soluble in alcohol, insoluble in chloroform, acetone and ether. (Found : $Cl = 17.2$. $C_{10}H_7ON_2Cl$ requires $Cl = 17.19$ per cent.).

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Pseudo-urethanes. Part I..

BY

HEMENDRA KUMAR SEN AND CHITTARANJAN·BARAT.

Some observations by one of us (Sen, Physics-Chemistry Colloquium, University College of Science, Calcuttà, August, 1924, *Proceedings of the 12th Indian Science Congress*, Benares, 1925, p. 113) relating to the mechanism of the pyruvic acid theory of alcoholic fermentation[*] have assumed more than speculative importance since

[*] Sen's scheme of alcoholic fermentation.

$$\cdots\rightarrow 2CH_3CHO + 2CO_2 \xrightarrow{\text{Reductase}} 2CH_3CH_2OH.$$
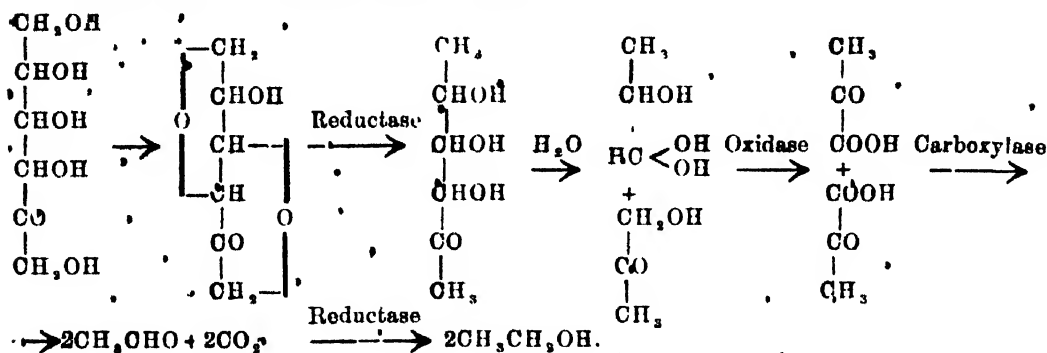
Graaff and Le Fevre's scheme based upon bacterial fermentation (*Bact. coli.* and *Bact. typhus* being employed) :—

$$CH_3 CH_2OH + CO_2$$
Alcohol.
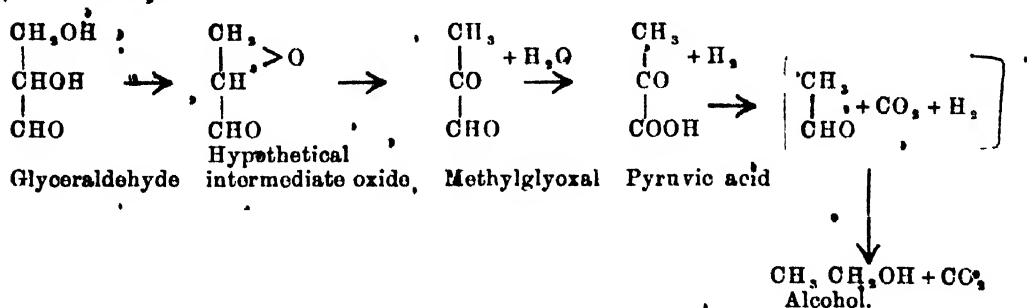
The amylene oxide structure given to glucose and fructose by Charlton, Haworth and Peat (*J. Chem. Soc.*, 1926, *129*, 89) lends itself also equally easily to convenient transformations by reductase according to the scheme mentioned above.

the publication of a fundamentally similar theory in February 1925 (*Biochem. Zeit.*, 155, 313) by Graaff and Le Fevre, who likewise regard the existence of an intermediate oxide in alcoholic fermentation as extremely probable.

The behaviour of the reductase in yeast, therefore, came to be critically examined with regard to its action on various types of compounds, as it is necessary for the validity of the oxide theory, suggested by one of us, that the reductase should be a sort of general reducing agent, capable of bringing about the reduction of ethers. When one notices that the double bond between carbon and oxygen in aldehydes. and ketones is prone to reduction by yeast, though no ethylenic linkage is yet known to have undergone similar change under like conditions, the question of configuration forces itself upon us. Some negative results obtained with chloral acetophenone, $CCl_3CH(OH)CH_2COC_6H_5$, in the course of this investigation establish the influence of configuration in such reductions, as chloral and acetophenone are already known to be susceptible of reduction by yeast. Further, the experiment leads to the very important conclusion that the yeast organism is less powerful as a dehydrating agent than the human organism which, according to Tappeiner (*Arch. exp. Path. und Pharm.*, 1894, 33, 364) causes it to lose its aldol phase, giving rise to trichlorethylidene acetophenone which is ineffective as a hypnotic. The behaviour of yeast towards hydracetylacetone, $CH_3 \cdot CH(OH)CH_2COCH_3$, and diacetone,

$$\begin{matrix} CH_3 \\ \quad \quad >C(OH) \cdot CH_2 \cdot CO \cdot CH_3, \\ CH_3 \end{matrix}$$
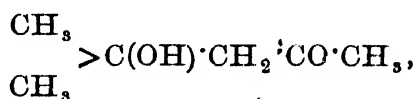
has, however, been found different, both undergoing splitting up or partial dehydration passing into ethylidene

acetone and mesityl oxide respectively. This decided stability of the aldol phase in chloralacetophenone and its homologues gave rise to the expectation that probably they would give formamide derivatives (urethanes) of modified hypnotic property. But although intermediate formamide derivatives have been isolated, as is described in the following pages, their constitution as simple urethane derivatives has come to be regarded with doubt for the reasons below.,

Chloralacetophenone, when treated with an excess of chloroformamide, yields almost quantitatively a compound of the same composition as

$$CCl_3 \cdot CH < \begin{array}{l} CH_2 \cdot CO \cdot C_6H_5 \\ O - CO \cdot NH_2 \end{array} \qquad (I).$$
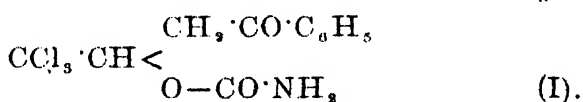
On crystallisation from hot absolute alcohol, the melting point diminishes steadily until it reaches a minimum. This product of minimum melting point was found to contain no nitrogen and to be trichlorethylidene acetophenone, $CCl_3 \cdot CH = CH \cdot CO \cdot C_6H_5$, obtained by Königs by the action of cold concentrated sulphuric acid upon chloral acetophenone (*Ber.*, 1892, **25**, 797). The true urethanes are stable in alcoholic solution, and they react with excess of chloroformamide so as to give rise to allophanic esters, thus :—

$$R \cdot O \cdot CO \cdot NH_2 + Cl \cdot CO \cdot NH_2 = RO \cdot CO \cdot NH \cdot CO \cdot NH_2 + HCl.$$
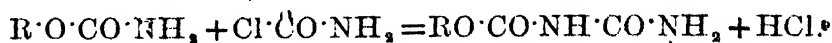
Thus, contrary to expectation, neither chloralacetophenone nor the supposed urethane derivative (I) gave any allophanic ester even with considerable excess of chloroformamide ; nor did benzaldehyde react with the chloroformamide compound of

chloralacetophenone to yield benzylidene diurethanes of the type--

$$C_6H_5CH< \begin{matrix} CCl_3 \\ | \\ NH\cdot CO\cdot OCH-CH_2\cdot CO\cdot C_6H_5 \\ NH\cdot CO\cdot OCH-CH_2\cdot CO\cdot C_6H_5 \\ | \\ CCl_3 \end{matrix}$$

(*Cf.* Bischoff, *Ber.*, 1874, 7, 628).
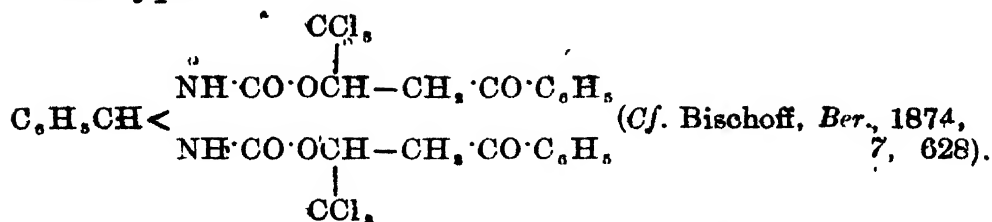
indicating the probable absence of a free NH_2 group. The conjecture, therefore, is that the suppored **urethane** (I) is a pseudo-urethane, having a metoxazine constitution (II).

$$CCl_3-CH \begin{matrix} CH_2 \\ \\ C(OH)\cdot Ph \\ \\ NH \\ CO \end{matrix} \quad O \qquad \text{(II)}$$
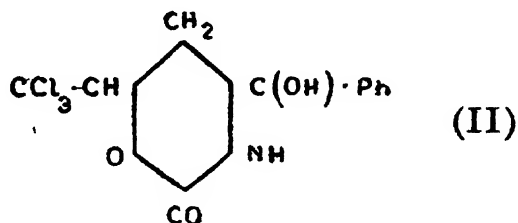
The action of chloroformamide was tried further on chloralacetone, chloralacetotoluone, chloral acetonaphthone and chloral acetoveratrone, and in each case, corresponding pseudo-urethanes were obtained, which upon heating with alcohol, gave trichlorethylidene derivatives, identical with those obtained by the action of concentrated sulphuric acid upon the chloral condensation products. These pseudo-urethanes decompose on melting, forming trichlorethylidene compounds, with the evolution of ammonia and carbon dioxide.

The investigation was extended, as already mentioned, to other compounds having similar aldol phase, *e.g.*, to hydracetylacetone and diacetone. These substances do not yield urethanes with chloroformamide, but readily form the ethylidene compounds by loss of the aldol phase, chloroformamide serving as a dehydrating agent. Thus from hydracetylacetone and diacetone, ethylidene acetone and mesityl oxide respectively were obtained.

It appears, therefore, that the CCl_3CHO group imparts a degree of stability to the aldol phase not met with in diacetone or hydracetyl acetone, and in fact on attempting to prepare benzaldehyde-acetophenone, $C_6H_5CH(OH)\cdot CH_2\cdot CO\cdot C_6H_5$, with glacial acetic acid as the condensing agent, benzylidene acetophenone was obtained, although with chloral under similar conditions, products with the aldol phase were uniformly isolated.

<div align="center">EXPERIMENTAL.</div>

<div align="center">*Chloralacetophenone and Chloroformamide.*</div>

Chloralacetophenone, $CCl_3.CH(OH).CH_2CO.C_6H_5$ was prepared according to the method of Köhigs (*loc. cit.*) by condensing chloral (freshly distilled) with acetophenone in the presence of glacial acetic acid. Nineteen g. of the crude condensation product were obtained from 10 g. of acetophenone. It was best purified from hot petroleum ether, using animal charcoal as a decoloriser; m. p. 68-70°. When this was treated with the molecular quantity of chloroformamide in dry ethereal solution, the product obtained was a mixture of the pseudo-urethane derivative and the unconverted chloral acetophenone. In order to effect a complete conversion, an excess of chloroformamide has to be employed, which is not prejudicial to the purity of the condensation product, as no allophanic ester is formed (*loc. cit.*). On mixing the ethereal solutions of chloroformamide and chloralacetophenone, no change of temperature was noticed; the mixture was allowed to stand about 15 minutes at room temperature, and then the ether was boiled off, the excess of chloroformamide decomposed with ice-water, and the pseudo-urethane obtained as a solid, insoluble in water. It can be crystallised by dissolving in *warm* methyl or ethyl alcohol and diluting with water, when it

separates as small prisms, m. p. 155° with decomposition. (Found : N = 4·7 ; Cl = 33·98. $C_{11}H_{10}O_3NCl_3$ requires N = 4·5 ; Cl = 34·3 per cent.).

The pseudo-urethane on being boiled with absolute alcohol for 2 hours, separates on addition of water as very pale yellow crystals melting at 102° which was found to be identical with trichlorethylidene acetophenone, prepared by the dehydration of chloral acetophenone ; a mixture of the two melted at 102°. (Found : Cl = 42·66. $C_{10}H_7OCl_3$ requires Cl = 42·7 per cent.).

The pseudourethane derivative with benzaldehyde and a drop of concentrated hydrochloric acid did not yield the benzylidene diurethane, although under similar conditions the formamide derivatives of both unsymmetrical and symmetrical dichlorisopropyl alcohol gave the corresponding diurethanes.'

Chloralacetotoluone.

Chloralacetotoluone, $CCl_3CH(OH)CH_2.CO.C_6H_4.CH_3$ was obtained from p-tolyl methyl ketone (7 g.) by condensation with chloral (8 g.) in the presence of glacial acetic acid (8 g.), in the same manner as chloral acetophenone. The heating on the sand-bath was continued for 15 hours, with a calcium chloride guard tube on the reflux condenser. The yield of crude chloral acetotoluone was about 7 g. It was purified by crystallisation from hot petroleum ether; yield 4 g; m. p. 100°. (Found : Cl = 37·4. $C_{11}H_{11}O_2Cl_3$ requires Cl = 37·8 per cent.)

The pseudo-urethane was prepared by treating an ethereal solution of chloral acetotoluone with an excess

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* Benzylidene diurethane of unsymmetrical dichlorisopropyl alcohol m.p. 135-36°. (Found : N = 6·5 ; Cl = 32·71. $C_{16}H_{18}O_4N_2Cl_4$ requires N = 6·48 ; Cl = 32·87 per cent.).

Benzylidene diurethane of symmetrical dichlorisopropyl alcohol, m.p. 160-162°. (Found : N = 6·71 ; Cl = 32·83. $C_{16}H_{18}O_4N_2Cl_4$ requires N = 6·48 ; Cl = 32·87 per cent.).

of an ethereal solution of chloroformamide as described before, m.p. 160° with decomposition. (Found: $Cl = 32.4$; $N = 4.4$. $C_{12}H_{12}O_3NCl_3$ requires $Cl = 32.30$; $N = 4.3$ per cent.).

Upon boiling the pseudo-urethane with absolute alcohol for 3 hours under a reflux condenser, a yellowish solid was obtained which on crystallisation melted at 88-90°. The trichlorethylidene acetotoluone prepared by the dehydrating action of sulphuric acid on chloral-acetotoluone melted also at 88-90° and so did a mixture of the two. (Found: $Cl = 40.05$. $C_{11}H_9OCl_3$ requires $Cl = 40.4$ per cent.).

Chloralacetonaphthone, $CCl_3.CH(OH).CH_2.CO.C_{10}H$. was prepared as before from α-acetonaphthone and chloral. The yield of α-acetonaphthone was very poor on following the method of Pampel and Schmidt (*Ber.*, 1886, *19*, 2898). It was therefore ultimately prepared by the method of Claus and Feist (*Ber.*, 1886, *19*, 3180) with an yield of 45 per cent. of the theory. The redistilled acetonaphthone (13.5 g.) was mixed with chloral (12 g.) and glacial acetic acid (12 g.), and the mixture was heated under a reflux condenser on the sand-bath for 18 hours. The resulting dark oil was repeatedly washed with hot water to remove chloral and acetic acid and the residue was dissolved in ether. The solution was dried by means of ignited sodium sulphate and filtered. The ether having been evaporated, the oily residue, was stirred with petroleum ether and the petroleum ether extract decanted. On continuing this operation several times, a brown solid weighing about 10 g. was left behind. The substance is very soluble in alcohol and was therefore purified by crystallisation from hot benzine, using animal charcoal as a decoloriser. After two recrystallisations the product was sufficiently pure, m.p. 90-92°. (Found: $Cl = 33.08$. $C_{14}H_{11}O_2Cl_3$ requires $Cl = 33.54$ per cent.)

Upon treatment with chloroformamide as usual, it gives a pseudo-urethane, m. p. 125° with decomposition. (Found : N$=4.04$; Cl $= 29.73$. $C_{15}H_{12}O_3NCl_3$ requires N$=3.88$; Cl $= 29.54$ per cent.).

On refluxing the compound with absolute alcohol for 2 hours, the trichlorethylidene acetonaphthone was obtained as a yellowish substance, m. p. 105-106°. (Found : Cl $= 35.17$. $C_{14}H_9OCl_3$ requires Cl$=35.56$ per cent.).

Chloral acetone, $CCl_3CH(OH).CH_2.CO.CH_3$ was prepared according to the method of Königs (*Ber.*, 1892, 25, 794) but the yield was exceedingly poor. By substituting 1 per cent. sodium carbonate solution for sodium hydroxide, the yield was better, but was considerably lower than that claimed by Königs. From 3.2 g. of acetone about 0.5 g. of the pure condensation product, m. p. 75-76°, was obtained. The pseudo-urethane prepared as usual melted at 98° with decomposition. (Found : Cl$=42.87$. $C_6H_8O_3NCl_3$ requires Cl$=42.84$ per cent.).

The yield was so poor that no further investigation could be carried out.

Chloralacetoveratrone, $CCl_3.CH(OH).CH_2.CO.C_6H_3$ $(OCH_2)_2$. An attempt was made to prepare veratrol from catechol according to Perkin and Weizmann's method (*J. Chem. Soc.*, 1906, 89, 1649) but without any success whatsoever. Accordingly it was prepared by the method of Marrasse (*Annalen*, 1869, 152, 74) from guaiacol. The yield was very satisfactory, about 85 g. of veratrol being obtained from 36.4 g. of guaiacol. The product boiled at 205-206°.

Acetoveratrone was prepared according to the method of Pictet and Gams (*Ber.*, 1909, 42, 2947). The yield was good. The boiling point, however, was 172-174° under 15 mm. as against 206° at 12 mm. given by the authors.[*]

[*] The melting point, however, was 49-50° as given by the authors.

On oxidation of the acetoveratrone by alkaline permanganate, veratric acid (m. p. 180°) was obtained which was compared with veratric acid from stock. The semicarbazone melted at 218-20° with decomposition. (Found: $N = 18 \cdot 1$. $C_{11}H_{15}O_3N_3$ requires $N = 17 \cdot 7$ per cent.).

Redistilled acetoveratrone (6 g.) was treated with chloral (5·1 g.) and glacial acetic acid (5·1 g.) and heated for 7 hours. The pasty mass obtained after washing with hot water was purified by repeated washing with petroleum ether; yield 6 g. As the substance is very sparingly soluble in benzine, it was crystallised from dilute alcohol by cooling with ice. The pure product was obtained after three crystallisations, using animal charcoal as decoloriser; yield 3 g., m.p. 120-22°. (Found: $Cl = 32 \cdot 46$. $C_{12}H_{13}OCl_3$ requires $Cl = 32 \cdot 2$ per cent.).

Considerable difficulty was experienced in preparing the pseudo-urethane derivative of chloralacetoveratrone. Even with marked excess of chloroformamide the condensation product was impure, melting between 80° and 100° and decomposing at 105-108°. Further investigation is proceeding in this direction.

Action of Chloroformamide on Hydracetyl Acetone.

Hydracetyl acetone, obtained from acetaldehyde and acetone in the presence of dilute potassium carbonate according to the method of Claisen (*Ber.*, 1892, 25, 3164), on being treated with chloroformamide in cold ethereal solution, evolved much hydrochloric acid and heat. The ether being expelled, the residue consisting apparently almost entirely of solid ammonium chloride, was treated with ice water when an oil was left. This was extracted with ether and the ethereal solution dried by ignited sodium sulphate and evaporated. The remaining oil boiled at 122°, the boiling point of ethylidene acetone.

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Action of Chloroformamide on Diacetone.

Diacetone, prepared by the condensation of acetone in the presence of calcium hydroxide according, to the method of Hoffmann (*J. Amer. Chem. Soc.*, 1909, *31*, 723) and treated as above with chloroformamide, gave an oil, b. p. 130°, which had the characteristic odour of mesityl oxide. A semicarbazone prepared in the usual way, melted at 128°. Mesityl oxide prepared by Freer and Lachmann's process (*Amer. Chem. J.*, 1897, *19*, 887) gave a semicarbazide, m. p. 126-128°. A mixture of the two melted at 128°, indicating that the two products were identical.

DEPARTMENT OF APPLIED CHEMISTRY,

UNIVERSITY COLLEGE OF SCIENCE,

CALCUTTA.

Preparation of Formaldehyde by the Dehydrogenation of Methyl Alcohol : A Study of Various Catalysts.

Part I.

By

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and

Jagat Bandhu Baksi

The technical processes for the preparation of formaldehyde are based on the fractional combustion of methyl alcohol, mostly with prepared copper as catalyst. The investigations of Sabatier and Mailhe (*Ann. Chim. Phys.*, 1910, *344*, 20), Orloff, (*J. Russ. Phys. Chem. Soc.*, 1907, *39*, 855, 1023, 1414; 1908, *40*, 7), Leblanc and Plasche (*Zeit. Elektrochem.*, 1911, *17*, 45) have proved that the first stage of the reaction consists in the dehydrogenation of methyl alcohol according to the equation,

$$CH_3OH = HCHO + H_2.$$

"Unfortunately, in the case of methyl alcohol, copper appears rapidly to lose its activity, either owing to the gradual reduction of unchanged cuprous oxide in solid solution in the metal, which may be the real effective catalytic agent, or for some other cause as yet unknown" (Rideal and Taylor, "Catalysis in Theory and Practice," p. 128). But if the hydrogen is removed by combustion with air the catalytic activity of copper is maintained steady.

In this investigation, our aim has been to obtain a catalyst which will have a high and steady dehydrogenating capacity,thus enabling formaldehyde to be prepared on a large scale by the dehydrogenation of methyl alcohol. The process has the advantage that hydrogen is obtained as a by-product, which has a high calorific value of 68,000 cals. per gram molecule, whereas the process of dehydrogenation of methyl alcohol is an endothermic one requiring only 12,000 cals. per gram molecule (approximately).

EXPERIMENTAL.

The experimental arrangement will be clear from Fig. 1. Pure methyl alcohol was boiled in a flask, with a side tube, by immersion in a thermostat. In order to ensure steady and constant evaporation of alcohol, the level of alcohol in the flask was always kept constant. The vapours passed into a long reaction tube, placed inside an electric furnace, with the catalytic material at the middle of the tube. The quantity of methyl alcohol passing over into the reaction tube was found to be 16 c.c., 21 c.c., and 28 c.c., per hour when the temperature of the evaporating bath was 68°, 68°·5, and 69° respectively. The furnace was maintained at a constant temperature by regulating the resistance. To prevent methyl alcohol condensing inside the tube, before entry into the furnace, the delivery tube was wound round with a manganin wire and maintained at about 100° by passing an electric current. The temperature was read off by means of a thermometer placed in contact with the catalytic material. The outflow gases were passed through two condensers as shown in the diagram and finally collected in a Hempel gas burette for analysis.

Fig. 1.
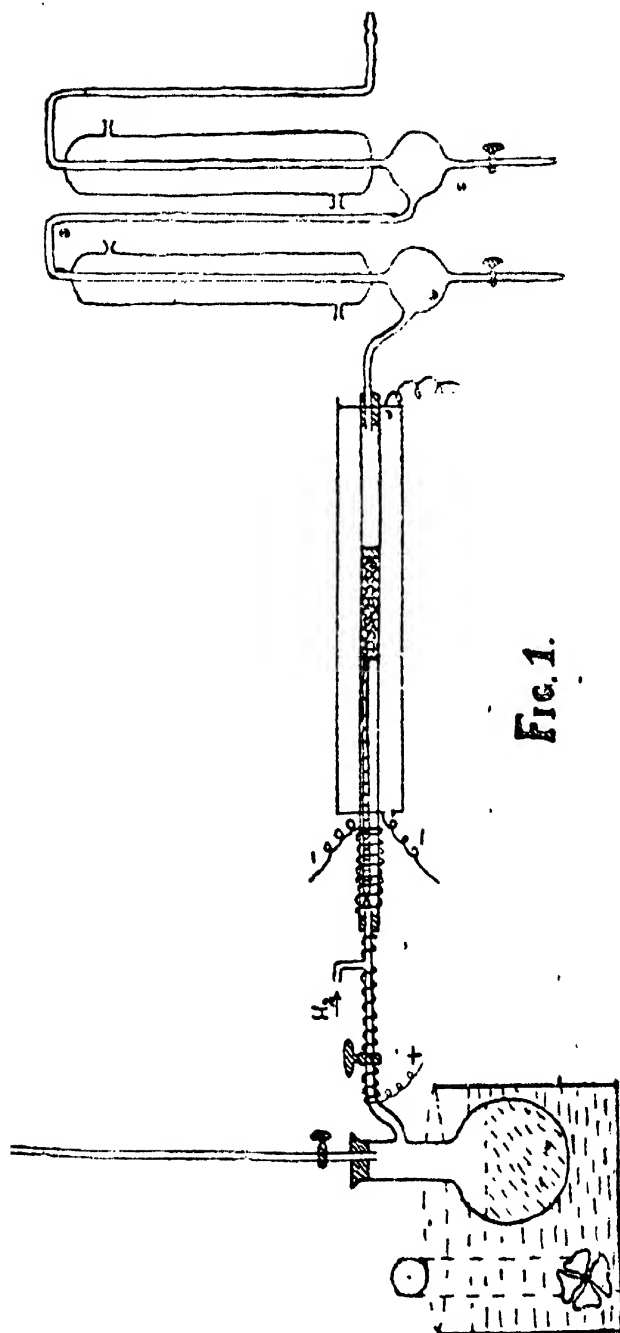
Experimental Data with Copper Catalyst in Presence of various Promoters.

Catalyst No. 1.

A solution of Merck's pure copper acetate was precipitated with excess of caustic soda (Kahlbaum), the precipitate thoroughly washed with distilled water and then dried in an oven at 110.° Eighteen gm. of this material in the form of powder were packed between asbestos fibres and reduced at 180° in a slow current of pure hydrogen for 48 hours. The catalyst was kept in an atmosphere of hydrogen in the intervals between two experiments. The data with this catalyst are recorded in Table I.

TABLE I.

Volume of catalyst space = 9·8 c.c.

Weight of catalyst = 18 gm. as oxide.

Temp. of furnace.	Temp of evaporation of MeOH or rate of evaporation of MeOH in c.c. per hour.	Total period of previous run at the time of collecting reaction products.	Space velocity-Vol. in c.c of gas mixture of CO₂, CO CH₄, and H₂ collected per c.c. of catalyst per hour.	ANALYSIS OF GAS.				Liquid mixture of MeOH and formaldehyde collected per hour in c.c.
				% CO_2	% CO	% CH_4	% H_2	
180°	70·5° or 50 c.c. per hour.	2 hrs.	943	3·1	7·8	2·2	86·6	...
,,	,,	3 hrs. 45 min.	687	5·0	3·8	3·8	87·0	...

After 5 hours' work the activity of the Catalyst No. 1 was found to diminish slowly but regularly. It was felt that the catalyst being in the form of powder was susceptible to "channelling" and the diminished activity might

be due to methyl alcohol vapour passing through some fixed pores whose walls might have lost their activity. Catalyst No. 2 was obtained in the form of pills in order that the effect of channelling, if any, might be eliminated.

Catalyst No. 2.

Copper oxide (5·5 g.) obtained from pure copper acetate was made into a large number of small pills when still in the moist state by the clean hand with the application of minimum pressure and reduced as before.*

Table II.

Volume of catalyst space = 2·6 c.c.

Weight of catalyst = 5·5 g. as oxide.

Temp. of furnace.	C. c. of MeOH introduced per hour.	Time of collection after start.	Space velocity.	ANALYSIS OF GAS				Undecomposed MeOH collected per hour
				% CO_2	% CO	% CH_4	% H_2	
180°	50	30 min.	1039	1·8	3·1	2·7	92·0	27·6
,,	37	2 hrs.	1016	3·6	2·7	4·1	89·0	11·25
190°	28	4 hrs. 40 min.	1431	2·0	5·4	3·4	89·1	8·0

* A pellet making machine could not be used, as the compressed pellets of CuO, after complete reduction, were found to have surprisingly small activity, and even then the activity diminished rapidly. It is clear that catalysis being a surface reaction the essential condition for a good catalyst is a loose spongy structure which is not attained if pressure is used in making pellets. It may be mentioned here that if the oxide material when almost dry, is broken up into small bits and only those particles which passed through a 10-mesh sieve but not through a 20-mesh sieve, were used as catalyst after reduction, the results obtained are identical with catalyst made into small pills by hand.

This catalyst appeared very promising as it retained its activity undiminished for 6 hours, and experiments were continued with a fresh sample of a larger quantity of this catalyst (No. 3).

Catalyst No. 3.

Copper oxide (15·5 g.) obtained as before from copper acetate in the form of pills was packed in the reaction tube inside the furnace and reduced for twenty-four hours. Shrinkage was observed and the catalyst was re-packed and again reduced for 16 hours.

TABLE III.

Volume of catalyst space = 6 c.c.
Weight of catalyst = 15·5 g. of oxide.

Temp. of furnace.	C.c. of methyl alcohol introduced per hour.	Time of collection, after start.	Space velocity.	ANALYSIS OF GAS.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
190°	28	50 min.	1040	1·5	2·7	3·1	92·9	10
195°	,,	3 hrs. 20 min.	1170	2·2	6·9	3·3	87·4	6
,,	,,	12 hrs. 30 min.	1170	3·2	8·5	3·4	85·0	6
,,	,,	15 hrs.	900	3·1	7·2	3·5	86·0	7·5
,,	,,	21 hrs. 20 min.	660	3·0	7·8	3·2	85·8	8

The activity of this catalyst remained undiminished for 17 hours and thereafter it began to fall until at the 22nd hour the activity became about half of the initial value. The yield of formaldehyde per c c. of catalyst

space per hour can be easily calculated. Now methyl alcohol and formaldehyde decompose thus :

$$CH_3OH = H_2 + HCHO \qquad (1)$$
$$HCHO = CO + H_2 \qquad (2)$$
$$2HCHO = CO_2 + CH_4 \qquad (3)$$
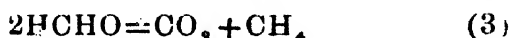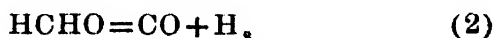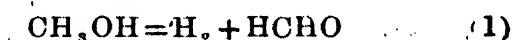
The amount of formaldehyde left undecomposed therefore is equivalent to $(H_2 - 2CO - 2CH_4)$. The data marked, with (*) in Table III therefore indicates that the yield of formaldehyde per hour per c.c. of catalyst

$$= 1040 \times \frac{92 \cdot 9 - 2 \times 2 \cdot 7 - 2 \times 3 \cdot 1}{100}$$

$$= \frac{1040 \times 81 \cdot 3}{100} \quad = 846 \text{ c.c. gaseous formaldehyde.}$$

The yield is satisfactory but unfortunately the catalyst was not very long-lived. Again, the quantity of liquid collected in the condensers which was mostly methyl alcohol, remaining undecomposed after passing over the catalyst, was not negligible. For successful industrial application, experimental conditions should be so chosen that the quantity of undecomposed methyl alcohol should become negligible. This can be achieved by raising the temperature of the catalyst, which, however, unfortunately has the effect of increasing considerably the decomposition of formaldehyde according to the equation $HCHO = CO + H_2$.

It was hoped that with the aid of promoters impregnating the copper catalyst, the desired end may be achieved. Before attempting to stabilise and enhance the activity of this catalyst by promoters, an investigation was made with various forms of copper catalyst in the pure state.

Catalyst No. 4.

Copper oxide (28·5 g.) obtained in the form of pills from copper sulphate by precipitation, with caustic soda was taken.

TABLE IV.

Volume of catalyst space = 10·6 c.c.

Weight of catalyst = 28·5 g. as oxide.

Temp. of furnace.	C.c. of methyl alcohol introduced per hour.	Time of collection after start.	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195°	28	1 hour.	402	3·0	0·8	3·0	93·0	16
,,	,,	6 hours.	282	2·8	0·7	2·9	93·2	12

The initial activity of Catalyst No. 4 is $\frac{1}{4}$ of that of No: 3 and even this small activity rapidly diminishes till at the end of the 6th hour it has dropped to about 1/5th. The catalyst was discarded as unsuitable for investigation. No trace of sulphur could be detected chemically in this catalyst and the method of preparation was exactly the same as for Catalyst No. 8. It is strange that the catalytic activity of Catalyst No. 4 should be so entirely different from that of No. 3. In all future investigations, therefore, copper obtained from copper acetate was used as the catalyst base to which various promoters were added.

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Catalyst No. 5.

Copper acetate (60 g.) and nickel acetate (0·3 g.) were dissolved together in a large quantity of water and precipitated with excess of caustic soda under constant stirring. This oxide (13·6 g.) made into small pills by the clean hand and reduced for 48 hours formed Catalyst No. 5.

TABLE V.

Volume of catalyst space $= 6·9$ c.c.

Weight of catalyst $= 13·6$ g. as oxide.

Temp. of furnace.	C.c. of methyl alcohol introduced per hour.	Time of collection after start.	Space velocity	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195°	28	4 hours	1218	2·8	10 5	2 8	84·0	4
,,	,,	10 hours.	1113	3·0	9·2	2·8	84·5	·85
,,	,,	10 hrs. 45 mins.	860	2 9	9·6	3·1	84·2	15

The Catalyst No. 5 (100 g. copper acetate : 0·5 g. nickel acetate) at first proved successful, for the space velocity was 1218, and the undecomposed methyl alcohol per hour about 4 c.c. as against space velocity, 1170 and liquid collection of 6 c.c. per hour in the case of Catalyst No. 3, which did not contain any promoter. But this activity is short-lived, falling to $\frac{2}{3}$ of its initial value in 11 hours. The quality of this catalyst did not improve by increasing the nickel content (100 g. copper acetate : 1 g. nickel acetate), as the percentage of CO in the issuing gases rose from 10·8 to 13·6 indicating a larger

percentage decomposition of formaldehyde. The space velocity did not increase nor was the activity of the catalyst of longer duration.

Catalyst No. 6.

For this set of catalysts silver was used as promoter, but the results were disappointing. This is rather surprising as the investigations of Bouliard (F. P. 412501/1910), Blank (*J. Soc. Chem. Ind.*, 1911, 30, 49) and Hochstetter (B. P. 464/1914) have shown that silver is the best catalyst for the manufacture of formaldehyde by the fractional *combustion* of methyl alcohol. It appears that silver is effective as a dehydrogenating catalyst only when its surface is maintained in an active state by the combustion of hydrogen with oxygen of air to form steam. Silver acetate (0·07 g.) and copper acetate (70 g.) were dissolved together and the oxide was precipitated with caustic soda, sieved when almost dry between 10 and 20 meshes and reduced for 48 hours.

TABLE VI.

Catalyst No. 6 (a). (CuAc : AgAc :: 100 : 0·1).

Volume of catalyst space = 8·2 c.c.

Weight of catalyst = 16 g. as oxide.

Temp. of furnace.	C.c. of methyl alcohol introduced per hour.	Time of collection after start	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
190°	28	1 hour.	600	4·4	3·0	2·6	90·0	9
,,	,,	9 hours.	454	4·7	4·5	3·0	87·6	7

Catalyst No. 6 (b).   (CuAc : AgAc :: 100 : 0·5).

Volume of catalyst space = 7·4 c.c.

Weight of catalyst = 15·8 g. as oxide.

Temp. of furnace.	C.c. of methyl alcohol introduced per hour.	Time of collection after start.	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195°	28	1 hour.	773	2·9	9·6	2·7	84·8	4·6
"	"	7 hours.	584	3·2	12·0	·3·6	80·6	16·6

Catalyst No. 6 (c).   (CuAc : AgAc :: 100 : 5).

Volume of catalyst space = 7 c.c.

Weight of catalyst = 16·3 g. as oxide.

Temp. of furnace.	C.c. of methyl alcohol introduced per hour	Time of collection after start.	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195°	28	1 hour.	275	1·7	12·2	2·6	83·2	13

It will be observed that the efficiency of the Catalyst No. 6 (a) is about half of that of pure copper catalyst. The stability is also less. With increasing quantity of silver as promoter, the catalyst became worse for our purpose in that the percentage of CO in the outflow gases correspondingly increased.

Catalyst No. 7.

In this set of catalysts, thorium oxide was used as promoter. Catalyst No. 7 (a) consisted of the reduced material from 16 g. of the oxide sieved between 10 and 20 meshes, obtained from a mixture of copper acetate and thorium nitrate in the ratio of 100 to 1. Catalyst No. 7 (b) being the same as above but the ratio of copper acetate to thorium nitrate was as 100 : 0·2. Catalyst No. 7 (c) consisted of the reduced material obtained from 32 g. of oxide, the ratio of copper acetate to thorium nitrate being 100 : 0·1.

TABLE VII.

Catalyst No. 7 (a).

Volume of catalyst space = 11·7 c. c.

Weight of catalyst = 16 g. as oxide.

Temp. of furnace.	C. c. of methyl alcohol introduced per hour.	Time of collection after start.	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO₂	% CO	% CH₄	% H₂	
195°	21	10 hrs.	1169	1·9	15·4	3·4	79·2	2·5
180°	,,	37	964	3·1	17·5	3·8	75·3	3
,,	,,	54	985	3·2	12·2	3·5	80·5	2

Catalyst No. 7 (b).

Volume of catalyst space = 10 c .c.

Weight of catalyst = 16 g. as oxide.

Temp of furnace.	C. c. of methyl alcohol introduced per hour.	Time of collection after start.	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195°	21	8 hrs.	1584	2·4	6·4	2·4	89·0	5
,,	,,	17	1560	2·1	3·6	3·3	91·0	4
205°	,,	35	1584	1·8	6·0	4·0	87·8	3
215°	16	50	1536	2·6	13·2	5·2	78·5	1

Catalyst No. 7(c).

Volume of catalyst space$=18·6$ c.c.

Weight of catalyst $=16$ g. as oxide.

Temp. of furnace.	C. c. of methyl alcohol introduced per hour.	Time of collection after start.	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195°	28	26 hrs.	967	2·0	5·5	3·1	89·0	8
205°	,,	32	1224	2·4	4·8	2·3	90·0	4
,,	21	35	900	2·4	4·5	2·5	90·0	1·2

A few of the typical data with thoria as promoter are given in Table VII. The following conclusions are at once reached : (1) The catalysts retained their activity unimpaired for an almost indefinite time. (2) When approximately the same amount of catalyst-material is used, the activity of Catalyst No. 7(a) (1% thorium nitrate) is about the same as that of pure copper catalyst but that of No. 7(b) (0·2% thorium nitrate) is 1·5 times greater. (3) With increasing quantity of thorium nitrate,

decomposition of formaldehyde into CO and H_2 increases considerably and the suitability of the catalyst for the large scale production of formaldehyde correspondingly diminishes. (4) With increase in temperature, the quantity of undecomposed methyl alcohol diminishes but the percentage decomposition of formaldehyde into CO and H_2 increases. (5) Catalyst No. 7(c) (0·1% thorium nitrate) was obtained from 32 g. of the oxide material as against 16 g. in No. 7(b) and gave 18 litres of outflow gases per hour as against 15 litres from Catalyst No. 7(b). The space velocity was of course less but the total yield was greater. The quantity of undecomposed methyl alcohol was only 1·2 c.c. per hour when the furnace temperature was 205° and evaporating temperature 68°·5. The calculated yield of formaldehyde per hour was

$$= \frac{18,000 \times [90 - 2(4·5 + 2·8)]}{100}$$

$=13,000$ c.c. or approximately 15 g., the quantity of methyl alcohol introduced being $21 \times 0·8 = 16·8$ gm.

It thus appears that the problem of a suitable catalyst, for the continued dehydrogenation of methyl alcohol to yield formaldehyde is solved by using thoria as promoter to the extent 0·1 g. thorium nitrate in 100 g. of copper acetate.

Catalyst No. 8.

The success of thoria as promoter naturally suggested the use of ceria, and the results obtained were even more satisfactory. Cerous nitrate · (0·7 g., Kahlbaum) and copper acetate ·(70 g.) were precipitated together with pure caustic soda and the catalyst prepared in the usual way. This constituted ·Catalyst No. 8(a). In Catalyst

No. 8(b) the ratio of copper acetate to cerous nitrate was as 100 : 0·2 and in catalyst No. 8(c) the ratio 'was 100 · 0·1. The experimental data are given in Table VIII.

TABLE VIII.

Catalyst No. 8(a).

Volume of catalyst space=11·3 c.c.

Weight of catalyst=16 g. as oxide.

Temp. of furnace.	C. c. of methyl alcohol introduced per hour.	Time of collection after start (in hours).	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195°	21	7	1816	1·9	21·7	3·7	72·5	3
190°	16	17	1594	2·7	16·1	3·6	77·6	2·7
180°	„	25	1275	1·8	12·5	4·7	80·8	2·5
„	„	36	1275	1·8	11·8	5·0	81·3	2·5

Catalyst No. 8(b).

Volume of catalyst space=9·6 c.c.

Weight of catalyst=16 g. as oxide.

Temp. of furnace.	C. c. of methyl alcohol introduced per hour.	Time of collection after start.	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195°	21	15 hrs	1550	2·0	3·9	4·7	88·9	3·5
„	16	24	1275	2·0	3·8	4·6	89·5	2
„	„	45	1300	2·8	4·8	3·5	88·4	1·5
200	„	56	1375	2·6	5·2	3·1	88·9	1·5

Catalyst No. 8(c).

Volume of catalyst space $= 8.8$ c.c.

Weight of catalyst $= 16$ g. as oxide.

Temp. of furnace.	C. c. of methyl alcohol introduced per hour.	Time of collection after start.	Space velocity.	Analysis of gas.				Undecomposed methyl alcohol collected per hour.
				% CO_2	% CO	% CH_4	% H_2	
195	16	12 hrs.	1637	3·7	5·1	3·7	87·5	2
··	··	25	1637	3·3	2·6	3·7	90·0	2·5
200	··	32	1774	3·2	4·5	3·8	88·5	2
··	··	36	1774	3·2	5·0	2·8	89·0	1·5

It will be noticed that for all these catalysts the space velocity increased with increase in furnace temperature; in the case of Catalyst No. 8 (a), an increase in temperature from 180° to 195° increased the subsidiary decomposition of formaldehyde considerably, the CO percentage in the outflow gases rising from 12 to 22 per cent. approximately. For catalyst with lower ceria content, this subsidiary decomposition is much smaller and is not very sensitive to small changes in temperature. It will also be observed that under similar experimental conditions, the efficiency of the Catalyst No. 8 (c) is at least 25 per cent. greater than that of Catalyst No. 8 (b) with double ceria content. The rate of formation of formaldehyde per hour by Catalyst No. 8 (c) at 200°, when the evaporating bath for methyl alcohol is at 68°, is

$$\frac{8.8 \times 1774 \ (89 - 16)}{100} \quad \text{or } 11,000 \text{ c.c. approxly.}$$

or 12·5 gm., the quantity of methyl alcohol introduced being 12·8 gm. The conversion is therefore, almost quantitative. This catalyst is more efficient than Catalyst No. 7 (c) (with 0·1 per cent. thorium nitrate) as with half the catalyst material almost similar quantity of formaldehyde is produced.

Our best thanks are due to Mr. B. S. Srikantam, M.Sc., who carried out some preliminary experiments on this subject.

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